TIGHT BINDING BOOK

PROCEEDINGS

OF THE

INDIAN ASSOCIATION

FOR THE

CULTIVATION OF SCIENCE

VOL. III.

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1917.

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PLATES.

PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

Vol. III. No. 1.

Saturday, February 24th, 1917 at 5 P.M. Dr. B. L. Chaudhury, D.Sc., F.L.S., F.R.S.E., Vice-President, in the chair.

Notes on a Free living Amœba of a new Species.

BY RAI BAHADUR, DR. GOPAL CHANDRA CHATTERJEE, M.B.

Introduction.—In routine bacteriological exanimation of samples of potable water, I accidentally found a protozoa of identically the same species as the one I found previously in the intestinal contents of a diarrhœa case. It formed a subject of a paper I recently published. This stimulated me to make a study of protozœ fauna of potable waters with a view to 1stly isolation in pure state protozœally speaking of some of the easily culturable types and study them in all their phases in test-tube cultures so that it may serve to illuminate some of the obscure points in the life history of some of the allied parasitic forms, 2ndly to find out any particular species or group of species in any sample of water, presence of which may indicate possible fæcal contamination.

I entirely depended on cultural methods for separation and study of the protozœ. By these means, I have succeeded in isolating several types. One of these is an amœba which showed well marked characters by which it can be easily identified and differentiated from the previously known ones.

Description of the amœba.—It first came under my observation in ordinary peptone bouillion culture of a sample of water. In this it grew luxuriantly, a single drop of the broth showing millions of them. When examined under high power without staining, these were seen as small globular bodies floating about in the fluid. They showed very little amœboid movements. When examined carefully, the circular bodies showed change of shape and occasionally a slight protrusion of pseudopodia.

When stained by Giemsa stain, they show a body about 3 to 5 μ diameter. In the centre is situated a voluminous nucleus ; this shows a cluster of chromatic dots distributed throughout the nucleus without showing any differentiation of central caryosome and peripheral chromatic layer. No definite nuclear membrane can be made out in many specimens. The chromatic dots forming the nucleus are distributed throughout the protoplasm of the cell, so that a differentiated nucleus is not clearly seen. The protoplasm of the cell shows no vacuole no pulsating vacuole can be made out. It is uniformly stained.

Method of division—The dividing stage has been clearly followed by me in plate culture underneath the microscope. As a rule one amœba divides into two. The process takes from begining to complete

separation not more than 5 to 10 minutes. In stained preparation, no definite karyokinetic figure can be made out.

In some specimens, a large number of big-sized amœba are found which show the nucleus divided into 5 to 8 parts and distributed through several parts of the body of the amœba. This seems to suggest a process of schizogony but actual division into several amœbæ has not been observed by me.

Cyst or spore formation.—In several ordinary types of culture amœbæ found in water, they show a well marked tendency to form cyst on the third or fourth day of culture irrespective of supply of nutrition or of water—in fact this cyst formation is the rule. In this amœbæ I failed to find any cyst even after 10 days of culture in solid medium, After this time, they die out and disappear from culture whereas in the case of ordinary amœbæ they can be seen in solid medium even after two months though most of them have transformed themselves to the cystic stage.

Flagellate condition.—Under certain condition, which I could not make out, the majority of the individual amœba in culture transform themselves suddenly to actively moving flagellate condition. These when fixed and stained by Iron-Hematoxylin show a small oval body about 3μ length, showing clear protoplasm and a nucleus situated at one pole of the body. The nucleus show clear differentiation of a central caryosome and a clear zone outside it. In front of the nucleus are seen originating two flagella without the intervention of any basal granules.

Cultural characters.—This amœba shows a remarkable property of growing luxuriantly in ordinary agar used for cultivating bacteria and also in broth. In Frosch's medium, it also grows luxuriantly. In Musgrave's medium it grows scantly. On the surface of potato, the amœba grows very luxuriantly. When a film is made from potato culture, the amobœ are seen in various sizes, some being not bigger than $1{\cdot}5\mu$ while the biggest measures about 7 to 8μ.

Literature.—For the purpose of my paper, it will suffice if I deal with the papers dealing with the culturable free living amœbœ whose specific characters have been clearly defined. Of those the most important is by Nägler who described the characters of 7 varieties of amœbœ which he cultivated in Frosch's medium. All these amœbæ are much bigger than the one I have dealt with and all showed cyst formation very readily. Wherry isolated an amœba from water and studied it for 2 years. This showed endogenous budding and binucleated cyst formation. Besides this showed flagellate condition This is also much bigger than my amœbæ.

Vahlkampff describes characters of Amœba Simon. These all show cyst formation and pulsating vacuole.

From all these it appears that this amœba differs from all previously described ones by the following characters.

(1) The power of rapid growth in ordinary agar and potato,

(2) By its small size,

(3) Want of cyst formation.

Illustrations.

1. Plate No. I is made from 24 hours bouillon culture stained by Giemsa. The plate shows an actual field showing the large number of amœbæ. It is drawn under $\frac{1}{12}$ apochromatic lens and No. 6 eye-piece.

Plate No. II is a preparation from a plate culture in ordinary agar. Stained by Iron-hæmatoxylin drawn under $\frac{1}{12}$ apochromatic lens and No. 12 eye-piece.

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On the Process of Development of Rohita, Catla and Cirrhina Mrigala in confined Waters in Bengal.

BY BEPIN BEHARY DAS, M.A.

Introduction.

The principal and the most economic of the Bengal fresh water fishes of the carp family are the *Rohita, Catla, Cirrhina mrigala* and *Calbasu.* In Bengal, the मत्स्यदेश of ancient India, where rice being the staple food, fish eating was considered necessary by the Hindu *Sastrakars,* the culture of these fish was thought of as an important element in domestic economy. This culture was, however, entirely in the hands of fishermen who, though not a race of great erudition, was undoubtedly one of keen intellect and from whom originated the famous व्यासदेव and the renowned Pandavas and Kouravas. It is true that those of superior intellect under great paternal influence developed themselves into the greatest geniuses and Rajas but those who were left to their professional calling did not leave to posterity any written account of their work. It is therefore very unfortunate that no literature as to the mode of culture of fish in vogue in ancient times has been discovered. All that is known about their work is that fishes of the carp family were regularly stocked in household tanks from where

they could be easily fished for use. The practical methods in connection with the culture, it appears, have been handed down from father to son as is the case with most of artisan classes in India. From what could be gathered from the present generation of Bengal fishermen who command information of about one century back, it is clear, that they had no knowledge of the spawning habits of the fish like *Rohita*, &c., which form the subject matter of the present paper. Consequently no attempts were made to culture the fish by inducing them to spawn. It is however certain that the practical fisherman of Bengal attempted to find out whether it was possible to raise fry by the spawning of the fish in Tanks. There is also evidence of attempts for finding out the conditions under which the fish wonld spawn. The sum total of their knowledge in this direction is that these fish do not breed in tanks or in confined waters in Bengal, while the inferior members of the family Cyprinidæ do breed in confined waters. With our present knowledge about the spawning habits of these fish it will be wrong to reflect on the spirit of research of our fishermen. It was not for the practical fisherman to undertake such a work and he never felt any great necessity for such a knowledge in his culture of fish. In some cases local knowledge of great scientific value has been noticed and worked up to but there had been no attempt to publication. This is due mostly to the poor condition of the fishermen—they, being pressed very hard for the bare necessities of life, were unable to think of anything beyond what brought them something to go on with.

" In cool sequestered vale of life
They led the noiseless tenor of their way."

In all cases the practical fishermen were able to obtain fry for his economic culture. This ready supply of fry from the rivers made him think of the spawning condition of the fish not as a thing of great importance in his culture. He, however, knows that the fish have roe in some cases and milt in others and that the ripening of the roe and the milt takes place once in one year *viz.*, in the rainy season. After the first showers when there is flood in the rivers tiny larval fish are fonnd in great numbers. These are collected by a very careful method devised by the fishermen themselves and cultured in small nursery tanks before they attain the shape and form of fish in the course of two weeks. There are a class of fishermen whose work is to nurse the larval fish for two weeks after which the small fry are caught by a fine net and sold to others who either stock the fish in larger tanks or who nurse them in a second system of tanks where they grow up to fingerlings in two months. These are then introduced into stocking tanks where the growth is a matter of chance ;—in some tanks the rate of growth is small, while in others it is extraordinarily great—depending chiefly on the natural nutrition of the tank.

Thus the system of culture in use in this country starts with the collection of the fry from rivers and ends with the stocking of the fingerlings in stocking tanks. There is no arrangement to examine the fish before it is taken out for consumption—and no rule to preserve it, if it is not fully grown. The fish is generally caught for the first and the last time in its life

and when once caught it is not allowed to retun to water even if it has not attained the adult stage. There is however a tendency to allow it to grow up as it is considered more profitable to kill it when adult than when it is young. This indiscriminate destruction of young fish is due partly to the pressing needs of the poor fishermen and also to the manner of leasing out the fisheries.

As the Tanks are mostly owned by the Zamindars and others who are not fishermen the fish culture in them is involved with some difficulty. The culturist in most cases has to take lease of the tanks and pay rent to the owners or the culture is done by the owners themselves. In the latter case the owners have to incur expenses for the purchase of fry and the cost of netting fry and the fish. In the majority of such cases the owners of the Tanks who might be called amature fish culturists do not sell their fish to the public but reserve them for their own use on extraordinary occasions and feasts. So that the fish produced by the amature culturists is not available for the regular consumer. On the other hand the fish produced by the fishermen is the source of a regular business which forms the means of livelihood of many of them. This fish forms a part of the fish supply in Bengal markets. The quantity however is very small and many of the fishermen engaged in the business complain of the small pofit. It is therefore clear that without an improvement in the method of culture, Pisciculture in tanks will cease to be of any use as regards the supply of fish to the public and also as regards a business by itself. The enquiry into Fishery

matters was undertaken by Sir K. G. Gupta and on his recommendation one student was deputed to study the culture of the Carps in Europe which are similar to our Rohita &c., and another for Shad in America which are similar to our Hilsa. The writer of the present paper was elected to study the culture of carps in European countries where the results have been very promising. The following account is a brief statement of the work undertaken by him since his return to India.

Experiments and Observations.

Soon after my return from Europe I arranged in March 1910 four tanks spawning experiments in Bhagalpur. These were not more than 10 *cottas* each in extent and were constructed by erecting small embankments in a sloping land. The site was in the Hathia-nullah in Barari, Bhagalpur. *Broodfish (Rohita, Catla* and *mrigal)* were collected from the river Ganges and also from the several tanks in and about Bhagalpur. These broodfish were with the exception of a few only not properly mature for reproduction and the mates were not exactly matched on account of the great scarcity of broodfish. But before any experiment could be tried the spawning tanks were filled up by an accident. This was on account of the slip of a huge bank of sand from the water-works. Thus no results were obtained in 1910-11.

My next attempt was at Berhampur in the District of Murshidabad. Arrangements were made for six spawning experiments with *Rohita, Mrigal* and *Calbasu.* Four of these were tried in four newly excavated tanks, 50 feet by 50 feet and 8 to 10 feet deep.

The other two experiments were tried in two old tanks which were cleared of the silt from the bottom and re-excavated for the purpose. Broodfish were collected from the Bhagirathee and Bhandardaha Beel as well as from some of the tanks in Kasimbazar and Polinda. In the selection of the broodfish great attention was paid to sexual maturity of the fish—only fully mature ones were taken for the experiment. There were no mature *Catla* found although more than 100 fish were examined. In this selection of the broodfish it was noticed that while in some tanks the *Rohita* and *mrigal* were found mature enough for reproduction, in others there was no development of the genitals although the fish were in an adult stage weighing 5 to 6 seers each. The same was the case with fish from the Bhagirathee and the Bhandardaha Beel. The development of the genitals of the fish under varied circumstances is a subject by itself and has not been properly studied. This is left alone for the present. I am gathering materials to work up this subject and hope to complete it in future. To return to our point, only fully mature fish were used for the experiments at Berhampore. The *Rohita* and *mrigal* weighed from 4 to 6 seers each and the *Calbasu* were from 1½ to 2 seers. In selecting the match (Spawning party) great attention was paid to make the males strangers to the females. This was done by putting together males of one tank or river with females from a distant place, e.g., the males from the Bhagirathee were put together with females from a tank in Polinda. This kind of mating is believed in Austrian and Bohemian culture stations to increase

the sexual attraction and enhance the breeding. This is also said to improve the breed.

During the collection of the broodfish the males were kept separate from the females and every care was taken to see that the fish did not get any way injured—not a single scale was allowed to come off. They were transferred from one tank to the other by means of large wooden barrels full of water and carried on bulluck carts. Only two fish were taken at a time in a barrel containing 70 gallons of water.

The experiments proper ware started in the second week of June. The ratio of the females to the males in a spawning party was not allowed to be less than 1 : 2 nor was it more than 3 : 4. In the course of five weeks from the starting of the experiments a large number of fry was discovered in five of the experimental tanks. These were found to be *mrigal* in three cases and *Rohita* in other two; while in the tank in which the *calbasu* were put no fry were observed.

The tanks were situated at a distance of one mile from where I stayed, I visited the tanks three or four times during the day while a watchman was on duty all the time near the Tanks. No spawning movement was noticed by me or the watchman. But after five weeks swarms of tiny fish were observed in the four new tanks and in one of the old tanks as stated above.

The fry were fed with powdered lumps of dried blood collected from the slaughter house. The fry got accustomed to this feeding like the trout fingerlings to minced liver in Europe, They also increased

fairly well. In two weeks they increased to one inch. Everything was going on in order and there was every hope of rearing the young fish to maturity. But on account of an accident nothing further could be done. On the 17th September, 1911, there was a very heavy rainfall continuing for three days at Berhampur. All the tanks and the adjoining drain which was in connection with the Bhagirahee formed one sheet of of water. The result was that all the fry were lost and none could not be reared to maturity.

The conclusion arrived at by these experiments was that the *rohita* and the *mrigal* under favourable circumstances do breed in still water of tanks. The spawning habits of the fish as also their spawning movements were however not studied, nor was it possible to study the development of the embryo in the egg.

I am very much thankful to the Hon'ble Maharaja Manindra Chandra Nandi of Cossimbazar and to Babu S. V. Sen, Zamindar, Khagra for rendering me valuable assistance in respect of collecting broodfish for these experiments and in a variety of ways.

During the following four years experiments were conducted by the Fishery Department in Berhampur, Cuttack and Bankipur under the direction of the Deputy Director of Fisheries. Fish from the rivers were used as broodfish. The results of these experiments led to no defenite conclusion regarding the breeding habits of the fish. In some cases the *catla* and the *mrigal* were supposed to have spawned from the presence of the fry in the tanks discovered afterwards but neither any observation about the

nature of spawning, nor any study about the embryonic development of the fry within the egg was done. It was decided that in still water the spawning of the fish in tanks is a matter of chance *i.e.*, under peculiar circumstances if the female fish sheds her ova directly when the male sheds his spermatozoon, fecundation takes place. The fish were considered to spawn only when there is a current. The work of the Fishery Department in this direction then consisted in obtaining the fry from the river and supplying them to the public at cost price.

In 1915 I tried to artificially fertilise the eggs of ***rohita***, *catla* and *mrigal* and subsequently to incubate them in Macdonald jars. In an experiment of this kind done at Berhampur in 1910 according to the report of Babu S. V. Sen, Zamindar, Khagra, a few fry were obtained. I however was unable to come to any conclusion about it because myself never proceeded with the incubation of the eggs which were considered to have been fertilised. I was able only to mix the ova which were obtained by a caesarian operation on the female with the milt which could be stripped out of the males. I was compelled to leave the products, which on account of a change in appearance was considered to have been fertilized, in charge of Babu S. K. Sen who after some time reported to have obtained a few fry. In 1915 I was able to make a series of experiments of a similar nature at Cuttack. More than 25 experiments were done by taking out the ova by cutting open the female fish and mixing them with the milt which was obtained by stripping the male. There was a change in the appearance of

the ova when it was mixed with the milt. As there was no development of the embryo on incubation in Macdoland jars and in hatching trays under different conditions, the change in the appearance of the ova was certainly due to the absorption of water which might contain a trace of some salt and not to any real fertilisation. In these experiments I was able to try only the *rohita* and *calbasu* from Tanks. It was our intention to try the river fish—but no mature males could be obtained for our experiments—all those caught in the Mahanuddy were fully spent.

The conclusion arrived at by these experiments was that the artificial fertilization of the ova of *rohita*, &c., was very uncertain on account of their gelatinous nature. For this reason stripping is not possible even when the first is ripe. The extraction of the eggs by opening the fish evidently does not give the ova which are really fit for fertilisation. These experiments were started from the 1st of July 1915 and all the male *rohita* and *mrigal* from the rivers were found to be fully spent. From this and from my previous observations on the development of the sexual organs of the fish it appears that in an adult fish (*rohita* &c.,) the ovaries and the testes start to develop from the middle of March and become fully ripe by the end of May. So that the breeding season commences early in June.

With this state of our knowledge about the breeding habits of the *rohita*, &c., I was lucky to find, that the exact nature of their spawning. I was present in the village Talbandi in June 1916 when the fish were actually spawning in a "Bandh." "Talbandi" is 13

miles from Garbetta in the District of Midnapur. The "Bandh" or the Embankment in this village was con-constructed about 25 years ago. The construction is very much like a large spawning tank in Bohemia. During the rains the water area extends over more than 50 *bighas* but in dry weather it reduces itself to 10 *bighas* or less. The embankment is at the foot of a sloping country mostly covered with a juungle of Sal trees. The slope is very gentle being less than 1 : 50. So that the banks were nearly flat except on the side in which the embankment was constructed in order to form the reservoir. The condition was very similar to that in the spawning tanks in Europe and also to that in my experimental tanks in Bhagalpur. Here therefore I got everything what I was looking for in my experimental spawning tanks; there was the embankment, very gentle slope of the side, the bed which had been exposed to the sun and air during the major part of the year, &c. And the most important thing in them was that there were the broodfish. The people also reported that these fish regularly spawn almost every year. One thing in this place was not similar to the European spawning tanks for carp. It was this that the sides were not overgrown with grass &c., to which the firstilised eggs stick as in the case of the eggs of the common gold fish. The original intention for the construction of the Reservoir was irrigation but they introduced in quantity of fry in order to get some fish as a bye-product. These ultimately grew up and started spawning. Near about this reservoir I erected temporary hatchery. There was an arrangement for working four Macdoland

hatching jars, two wooden hatching trays and the final waste water was introduced into an excavation in the earth 3 ft. × 2 ft. × 1½ ft. deep. The water from the last was allowed to flow out through a brass mesh.

Thus equipped I was watching the movement of the fish in the reservoir. In the afternoon of the 13th June 1916, I found that some of the fish were moving about but this movement could not be considered to be due to spawning. This movement ceased under cover of night. It was drizzling but there was no breeze. Towards morning rather a strong breeze started and the fish were seen in groups coming in very shallow water where it was only one foot deep. Some of the fish were lying quite flat on one side for a time then they ran about round and round not very far from a central spot where they again returned. The water was very much coloured on account of the washing of the laterite of the soil and for this reason the exact outline of the fish could not be seen when in motion. But when some of them were lying on one side as stated above the fish could be distinguished. I saw many times large *catla* fish which would be more than 25 seers each. The *mrigals* were seen with the *mrigals* at time but during the whole period, all the *rohita*, *mrigals* and *catlas* were moving together. The fish were not at all shy and could be taken without any trouble. In this heterogenous mixture the fish were touching one another and at times gathered together in heap. There were *boalis* in the reservoir and two of the breeding fish were attacked by the *boali*. In one case the *boali* was killed by the bystanders. The spawning started

at 4 A.M., in the morning and in one hour's time large numbers of fertilised ova were drifted to the banks which were at about 20 yards from the spawning centre. I collected some of these and started their incubation in my hatchery. The spawning continued till 8 A.M. There was no current of any kind either flowing into the Reservoir or out of it. The drizzling rain was so small that the water was getting soaked in the sand. The breeze however continued and became stronger. Many of the eggs on that account were thrown over the dry sand which formed the banks of the "Bundh." A good quantity of the eggs was thus lost. Those which remained in the water were collected by those who do business in fry or those who culture fish in tanks. I arranged to introduce water by earthenware pitchers in order to put back the eggs into water and thus a portion was saved. The eggs remained in water in any position as their density was nearly the same as that of water. As the spawning continued the eggs were drifted more and more and in larger quantities towards the shore. When the spawning ceased the water was full of eggs from a depth of three feet to the shore. For ten hours the eggs were not allowed to be disturbed. After that time the development of the embryo within the egg shell was perceptible. The spinal column was seen nearly surrounding the yolk sac. It was then that they considered the eggs to be ripe (ডিম পাকিয়াছে). The eggs were collected by men who came from the adjoining villages and also from distant places. The collection of the eggs started from 2 P.M., and continued till 6 P.M. The owners of the Bundh did not charge any price for the eggs

but they distributed them among the assembled mass in order to ensure even distribution as much as possible. The management in this distribution was difficult and riots were not very uncommon that day. The eggs were collected by dipping with an earthen or metallic vessel about one seer in capacity. When the eggs became scarce on account of constant dipping they used a fine cloth to gather them together. When they collected as much of the eggs as they could, the work in the Bundh was finished. They took away the eggs with water in earthen "Handis" and put them in small excavations in the earth. These were about 3 feet by 4 feet and 2 feet deep. Some of them were larger while others were smaller. They are called "Hapor" হাপর and are filled with rain-water collected from the low lying lands. The eggs remained there till they were 24 hours old in which time they hatched out. After the eggs had all hatched out the larval fry were collected by means of a fine cloth and put into another similar excavation filled with fresh water. The fry are then ready for sale to those, who culture fish in tanks. These people come from over 20 miles. The sale is very brisk for the first two or three days. It sometime continues for 15 days but after seven or eight days the fry become weak and begin to die for want of food. During this period the only work of the fry seller is to add fresh water to the pits or "Hapors" and to protect them from overheating by the direct rays of the sun.

In my extempore hatching I incubated the eggs (1) in Macdonald jars (2) in a glass aquarium (3) in Zinc and (4) wooden troughs. The incubating appara-

tus were put in series and a gentle current of water about 1·5 quarts per minute was made to pass through them. Fine brass mesh was put seperating the diferent incubating vessels. For want of proper equipment microscopic examination of the embryo could not be done during the successive stages on the spot. From an examination of a series of specimens preserved by my wife, I am able to work out the growth stages of the embryo within the egg and also when it hatched out. For want of time I not was able to study more than a few of these specimens in the laboratory of our Science Association which has been my home, my alma mater, my guide, philosopher and friend ever since the dawn of my intelligence I am studing there specimens which show the development of the fry up to one month and hope to present you a thorough account in the next meeting. The following is the description of the different stages as far as I was able to complete.

(1) First hour after spawning

(2) Twelve hours ,, ,,

(3) Sixteen hours ,, ,,

(4) Twenty four hours after spawning just before hatching.

The egg shell is not shown in figs. 2,3 & 4.

(5) Seventy six hours after spawning or two days after hatching, side view.

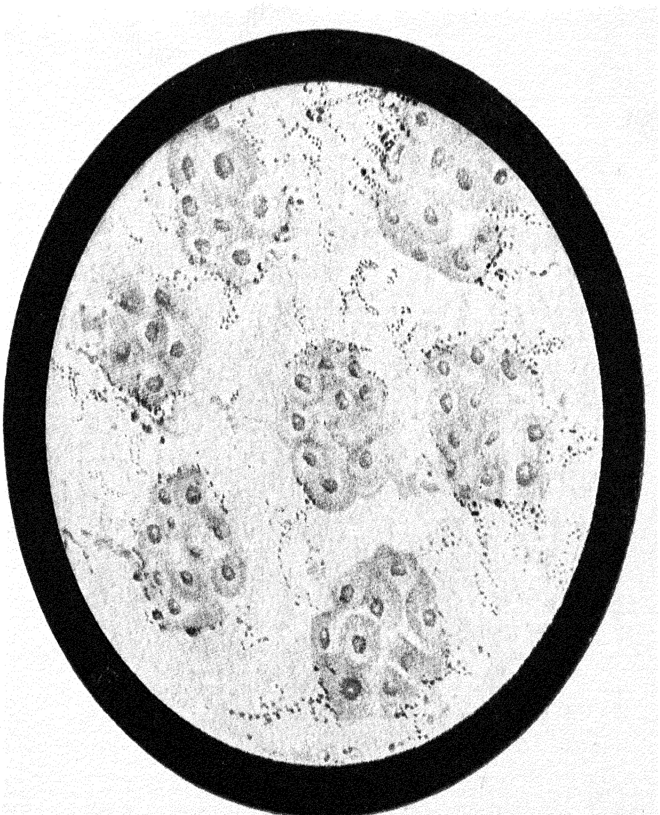
(6) Ditto, dorsal view.

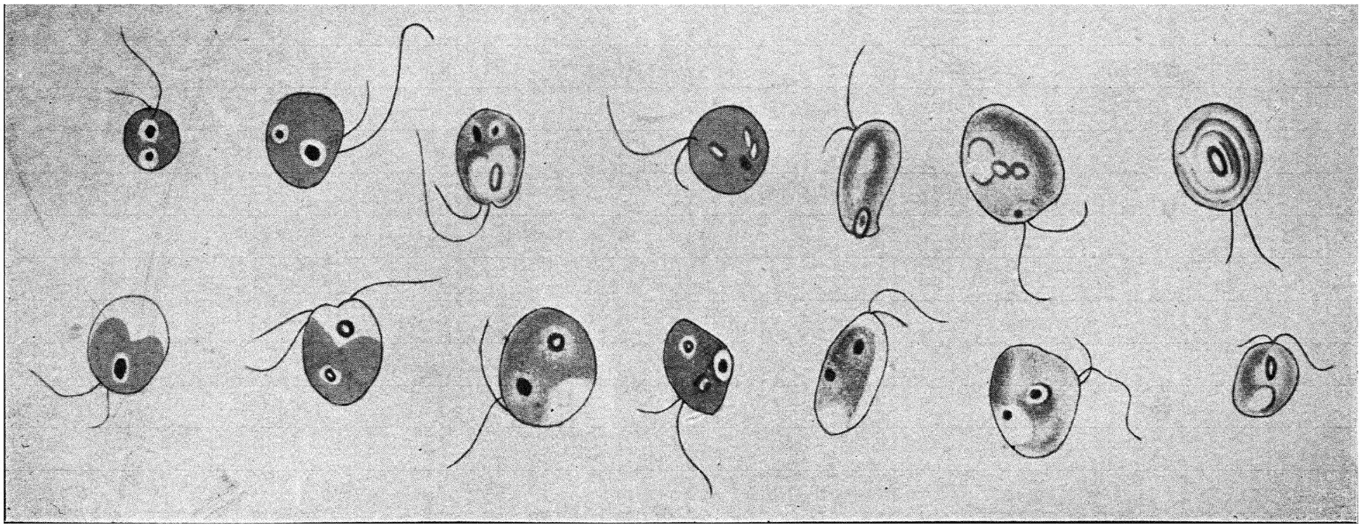
Further Experiments on Electrically maintained Vibrations.

BY C. V. RAMAN, M.A. and ASHUTOSH DEY.

(See Proceedings, Vol. II, Part I, 1916).

PLATE I.





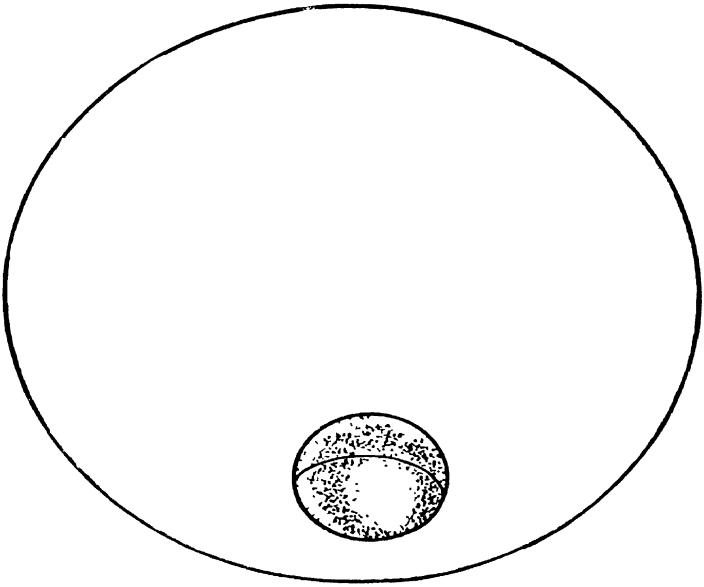


Fig. 1.

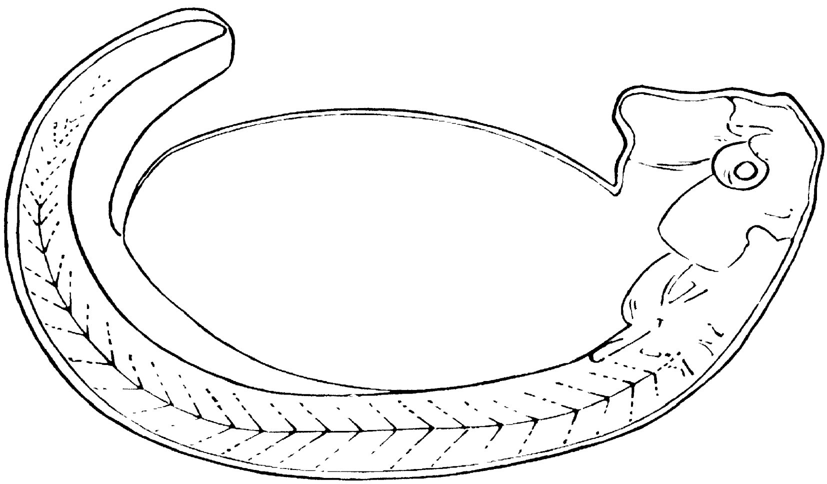


Fig. 2.

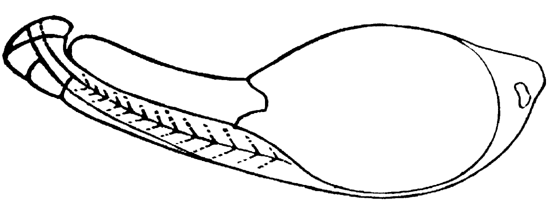


Fig. 3.

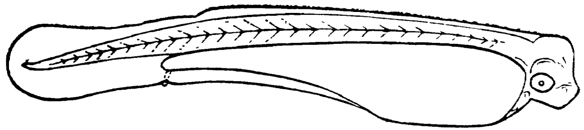


Fig. 4.


Fig. 5.


Fig. 6.

PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

Vol. III. Part II.

On Aerial Waves Generated by Impact*.

Part II.

By Sudhansukumar Banerjee, M.Sc.

1. Introduction.

The origin and characteristics of the sound produced by the collision of two solid spheres were discussed by me at some length in the first paper under the same title that was published in the Philosophical Magazine for July, 1916. It was shown in that paper that the sound is not due to the vibrations set up in the spheres, which, in any ordinary material, are both too high in pitch to be audible, and too faint in intensity, but to aerial waves set up by the reversal of the motion of the spheres as a whole. The intensity of the sound in different directions for the case, in which the two spheres were of the same material and diameter, was investigated by the aid of a new instrument which will be referred to as "the Ballistic Phonometer".† The intensity was found to be a maximum

* This is the complete paper of which an abstract was read at the Annual Meeting held on the 23rd of November, 1916. *Vide*, Report for the year 1915.

† This name was suggested by Prof. E. H. Barton, D.Sc., F.R.S., writing in the *Science Astracts*, page 399, Sept., 1916.

along the line of collision, falling off gradually in other directions to a value which is practically zero on the surface of a cone of semi-vertical angle 67° and rising again to a second but feebler maximum in a plane at right angles to the line of collision.

In view of the interesting results obtained for the case of two equal spheres, it was arranged to continue the investigation and to measure the distribution of intensity when the colliding spheres were not both of the same radius or material. A mathematical investigation of the nature of the results to be expected in these cases was also undertaken. In order to exhibit the results of the experiment and of the theoretical calculation, a plan has now been adopted which is much more suitable than the one used in the first paper. This will be best understood by reference to fig. 1 (Plate I), which refers to the case of two spheres of the same material and diameter.

This figure has been drawn by taking the point at which the spheres impinge as origin and the line of collision as the axis of x, and setting off the indications of the Ballistic Phonometer as radii vectores at the respective angles which the direction in which the sound is measured makes with the line of collision. The curve thus represents the distribution of intensity round the colliding spheres in polar co-ordinates, the points at which the intensity of the sound is measured being assumed to be all at the same distance from the spheres. The results are brought much more vividly before the eye by a diagram of this kind than by plotting the results on squared paper.

2. *Case of two spheres of the same material but of different diameters.*

Figure 2 (Plate II), which shows the observed distribution of intensity when two spheres of wood of diameters 3 inches and $2\frac{1}{4}$ inches collide with each other, is typical of the results obtained when the impinging spheres are nearly of the same density and are of different diameters. There is a distinct asymmetry about a plane perpendicular to the line of impact. In addition to the maxima of intensity in the two directions of the line of collision, we have the maxima in lateral directions, which are not at right angles to this line. The directions in which the intensity is a minimum are also asymmetrically situated.

For the explanation of these and other results, we have naturally to turn to the mathematical theory, which rests upon the fact that the sound is due to the wave-motion set up in the fluid by the sudden reversal of the motion of the spheres. Let a and b be the radii of the two spheres and ρ_a and ρ_b be their densities. Then the masses of the spheres are $\frac{4}{3}\pi\rho_a a^3$ and $\frac{4}{3}\pi\rho_b b^3$ respectively. Denoting the changes in velocity which the spheres undergo as a result of the impact by U_a and U_b respectively, by the principle of constant momentum we have $U_a : U_b = \rho_b b^3 : \rho_a a^3$. The ratio $U_a : U_b$ thus depends only on the diameters and the densities of the spheres, while, of course, the actual values of U_a and U_b would depend on the relative velocity before impact and the co-efficient of restitution. It is obvious that if we leave out of account the duration of impact, that is, regard the

changes in velocity of the spheres as taking place practically instantaneously, the character and the ratio of the intensities of the sound produced in different directions would be completely determined by the sizes of the spheres and the ratio of their changes of velocity, that is, by *their diameters* and *their masses*; when the spheres are of the same material, the nature of the motion in the fluid, set up by the impact, depends only on the radii of the spheres.

The complete mathematical problem of finding the nature of the fluid motion set up by the reversal of the motion of the spheres, taking the finite duration of impact into account, would appear to be of great difficulty. In my first paper, I have shown that when a single sphere of radius a undergoes an instantaneous change of velocity U, the wave motion produced is given by the expression

$$\psi = -\frac{\sqrt{2}\,Ua^3}{4}\frac{\partial}{\partial r}\left[\frac{e^{-\left(\frac{ct+a-r}{a}\right)}}{r}\cos\left(\frac{ct+a-r}{a}-\frac{1}{4}\pi\right)\right]\cos\theta, \qquad (1)$$

which indicates that it is of the damped harmonic type confined to a small region near the front of the advancing wave. The wave motion, set up in the case of two spheres in contact assumed to undergo instantaneous changes of velocity, would be of a more complicated type. In order to obtain a general idea of the nature of the results to be expected, particularly as to the intensity and character of the sound in different directions, we may consider the analogous acoustical problem of two rigid spheres nearly in contact, which execute small oscillations to and fro

on the line of their centres. This problem may be mathematically formulated and approximately solved in the following manner :—

Given prescribed vibrations

$$U_a \cos \theta_1 e^{ikct} \quad \text{and} \quad U_b \cos \theta_2 e^{ikct}$$

on the surfaces of two spheres of radii a and b, nearly in contact, it is required to determine the velocity potential of the wave motion started and the distribution of intensities round the spheres, where θ_1 and θ_2 are the angles measured at the centres A and B of the two spheres in opposite senses from the line joining the centres of the spheres.

Supposing now that an imaginary sphere is constructed, which is of just sufficient radius to envelop the two actual spheres (touching them externally), it is possible from a consideration of the nature of the motion that takes place in the immediate neighbourhood of the two spheres, to determine the vibrations on the surface of this imaginary sphere, which would produce on the external atmosphere the same effect as the vibrations on the surfaces of the real spheres A and B. When the equivalent vibration on the surface of the enveloping sphere has been obtained, we can, by the use of the well-known solution for a single sphere, at once determine the wave motion at any external point.

The radius of the enveloping sphere is evidently $a+b$, and its centre is at a point C, such that $BC=a$ and $CA=b$.

If the point C be taken as origin, and if the equi-

valent vibration on the surface of the enveloping sphere be expressed by the series

$$\Sigma A_n P_n (\cos\theta)\, e^{ikct}, \tag{2}$$

where A_n's are known constants, the velocity potential of the wave motion produced at any external point is given by

$$\psi = -\frac{(a+b)^2}{r} e^{ik(ct-r+a+b)} \Sigma \frac{A_n P_n (\cos\theta)}{F_n (ik.\overline{a+b})} f_n (ikr), \tag{3}$$

where

$$f_n (ikr) = 1 + \frac{n(n+1)}{2.\,ikr} + \frac{(n-1)\,n\,(n+1)\,(n+2)}{2.4.\,(ikr)^2} + \cdots$$
$$+ \frac{1.2.3\ldots 2n}{2.4.6\ldots 2n.\,(ikr)^n},$$

and

$$F_n (ikr) = (1+ikr) f_n (ikr) - ikr f_n' (ikr). \tag{4}$$

To obtain the equivalent vibrations on the surface of the enveloping sphere, we shall regard the small quantity of fluid enclosed by this sphere as practically *incompressible*, and use the well-known solution by the method of successive images for two spheres in an incompressible fluid.

We know that the velocity potential due to such a system of two spheres in an incompressible fluid can be expressed in the form

$$U_a \phi + U_b \phi', \tag{5}$$

where ϕ and ϕ' are to be determined by the conditions

$$\nabla^2 \phi = 0,\ \nabla^2 \phi' = 0,$$

$$\frac{\partial\phi}{\partial r_1} = -\cos\theta_1, \text{ and } \frac{\partial\phi'}{\partial r_1} = 0, \text{ when } r_1 = a,$$

$$\frac{\partial\phi'}{\partial r_2} = -\cos\theta_2, \text{ and } \frac{\partial\phi}{\partial r_2} = 0, \text{ when } r_2 = b,$$

r_1 and r_2 being radii vectores measured from A and B.

When ϕ and ϕ' have been determined so as to

satisfy these conditions the equivalent vibrations on the surface of the imaginary enveloping sphere can be taken to be very approximately given by

$$-\left[\mathrm{U}_a\frac{\partial\phi}{\partial r}+\mathrm{U}_b\frac{\partial\phi'}{\partial r}\right]_{r=a+b}^{e^{ikct}} \tag{6}$$

The functions ϕ and ϕ' as is well-known can be determined by the method of successive images and if the expressions for the velocity potential due to these images be all transferred to the co-ordinates (r, θ) referred to the centre C of the imaginary enveloping sphere, we easily obtain

$$2\phi=a^3\left[1-\frac{b^3}{(a+b)^3}+\frac{b^3}{(a+2b)^3}-\frac{b^3}{(2a+2b)^3}+\frac{b^3}{(2a+3b)^3}-\cdots\right]\frac{\mathrm{P}_1(\cos\theta)}{r^2}$$

$$+2a^3\left[b-\frac{b^3(a^2+ab-b^2)}{(a+b)^4}+\frac{b^3(2b^2-a^2)}{(a+2b)^4}-\frac{b^3(2a^2+ab-2b^2)}{(2a+2b)^4}+\frac{b^3(3b^2-2a^2)}{(2a+3b)^4}-\cdots\right]\frac{\mathrm{P}_2(\cos\theta)}{r^3}$$

$$+3a^3\left[b^2-\frac{b^3(a^2+ab-b^2)^2}{(a+b)^5}+\frac{b^3(2b^2-a^2)^2}{(a+2b)^5}-\frac{b^3(2a^2+ab-2b^2)^2}{(2a+2b)^5}+\frac{b^3(3b^2-2a^2)^2}{(2a+3b)^5}-\cdots\right]\frac{\mathrm{P}_3(\cos\theta)}{r^4}$$

$$+4a^3\left[b^3-\frac{b^3(a^2+ab-b^2)^3}{(a+b)^6}+\frac{b^3(2b^2-a^2)^3}{(a+2b)^6}-\frac{b^3(2a^2+ab-2b^2)^3}{(2a+2b)^6}+\frac{b^3(3b^2-2a^2)^3}{(2a+3b)^6}-\cdots\right]\frac{\mathrm{P}_4(\cos\theta)}{r^5}$$

$$+\text{etc.,} \tag{7}$$

$$2\phi'=-b^3\left[1-\frac{a^3}{(b+a)^3}+\frac{a^3}{(b+2a)^3}-\frac{a^3}{(2b+2a)^3}+\frac{a^3}{(2b+3a)^3}-\cdots\right]\frac{\mathrm{P}_1(\cos\theta)}{r^2}$$

$$+2b^3\left[a-\frac{a^3(b^2+ab-a^2)}{(b+a)^4}+\frac{a^3(2a^2-b^2)}{(b+2a)^4}-\frac{a^3(2b^2+ab-2a^2)}{(2b+2a)^4}+\frac{a^3(3a^2-2b^2)}{(2b+3a)^4}-\cdots\right]\frac{\mathrm{P}_2(\cos\theta)}{r^3}$$

$$-3b^3\left[a^2-\frac{a^3(b^2+ab-a^2)^2}{(b+a)^5}+\frac{a^3(2a^2-b^2)^2}{(b+2a)^5}-\frac{a^3(2b^2+ab-2a^2)^2}{(2b+2a)^5}\right.$$
$$\left.+\frac{a^3(3a^2-2b^2)^2}{(2b+3a)^5}-\ldots\right]\frac{P_3(\cos\theta)}{r^4}$$

$$+4b^3\left[a^3-\frac{a^3(b^2+ab-a^2)^3}{(b+a)^6}+\frac{a^3(2a^2-b^2)^3}{(b+2a)^6}-\frac{a^3(2b^2+ab-2a^2)^3}{(2b+2a)^6}+\right.$$
$$\left.\frac{a^3(3a^2-2b^2)^3}{(2b+3a)^6}-\ldots\right]\frac{P_4(\cos\theta)}{r^5}$$

$$-\text{etc.,} \qquad (8)$$

the law of formation of the series within the brackets being obvious.

Coming now to the present problem of two unequal spheres of the same material, let us take

$$a=2 \text{ inches and } b=1 \text{ inch.}$$

Since the change of velocities of the two balls is inversely proportional to their masses, we must have

$$U_b=8U_a.$$

Substituting the values for a and b we easily find that

$$2\phi=2^3\left[\left(1+\frac{1}{4^3}+\frac{1}{7^3}+\frac{1}{10^3}+\ldots\right)-\left(\frac{1}{3^3}+\frac{1}{6^3}+\frac{1}{9^3}+\cdots\right)\right]\frac{P_1(\cos\theta)}{r^2}$$

$$+2.2^3\left[1-\left(\frac{5}{3^4}+\frac{8}{6^4}+\frac{11}{9^4}+\frac{14}{12^4}+\ldots\right)-\left(\frac{2}{4^4}+\frac{5}{7^4}+\frac{8}{10^4}+\cdots\right)\right]\frac{P_2(\cos\theta)}{r^3}$$

$$+3.2^3\left[1+\frac{2^2}{4^5}+\frac{5^2}{7^5}+\frac{8^2}{10^5}+\ldots\right)-\left(\frac{5^2}{3^5}+\frac{8^2}{6^5}+\frac{11^2}{9^5}+\cdots\right)\right]\frac{P_3(\cos\theta)}{r^4}$$

$$+4.2^3\left[1-\left(\frac{5^3}{3^6}+\frac{8^3}{6^6}+\frac{11^3}{9^6}+\frac{14^3}{12^6}+\ldots\right)-\left(\frac{2^3}{4^6}+\frac{5^3}{7^6}+\frac{8^3}{10^6}+\cdots\right)\right]\frac{P_4(\cos\theta)}{r^5}$$

$$+\text{etc.,} \qquad (9)$$

$$2\phi'=-2^3\left[\left(\frac{1}{2^3}+\frac{1}{5^3}+\frac{1}{8^3}+\frac{1}{11^3}+\ldots\right)-\left(\frac{1}{3^3}+\frac{1}{6^3}+\frac{1}{9^3}+\cdots\right)\right]\frac{P_1(\cos\theta)}{r^2}$$

$$+2.2^3\left[\left(\frac{1}{3^4}+\frac{4}{6^4}+\frac{7}{9^4}+\cdots\right)+\left(\frac{4}{2^4}+\frac{7}{5^4}+\frac{10}{8^4}+\frac{13}{11^4}+\cdots\right)\right]\frac{P_2(\cos\theta)}{r^3}$$

$$-3\,2^3\left[\left(\frac{4^2}{2^5}+\frac{7^2}{5^5}+\frac{10^2}{8^5}+\frac{13^2}{11^5}+\cdots\right)-\left(\frac{1^2}{3^5}+\frac{4^2}{6^5}+\frac{7^2}{9^5}+\cdots\right)\right]\frac{P_3(\cos\theta)}{r^4}$$

$$+4.2^3\left[\left(\frac{1^3}{3^6}+\frac{4^3}{6^6}+\frac{7^3}{9^6}+\cdots\right)+\left(\frac{4^3}{2^6}+\frac{7^3}{5^6}+\frac{10^3}{8^6}+\frac{13^3}{11^6}+\cdots\right)\right]\frac{P_4(\cos\theta)}{r^5}$$

$$-\text{etc.} \qquad (10)$$

Summing the series we easily find that the prescribed vibration on the surface of the imaginary enveloping sphere

$$U_n\left[\frac{\partial\phi}{\partial r}+8\ \frac{\partial\phi'}{\partial r}\right]_{r=3\text{ ins.}} e^{ikct}$$

is proportional to

$$\left[\cdot 246\,P_1(\cos\theta)+3\cdot 180\,P_2(\cos\theta)-2\cdot 108\,P_3(\cos\theta)+3\cdot 5\,P_4(\cos\theta)+\text{etc.}\right]e^{ikct}.$$

We have seen that when the prescribed vibration on the surface of the imaginary sphere is

$$\Sigma\,A_n\,P_n(\cos\theta).\,e^{ikct},$$

the velocity potential of the wave-motion is

$$\psi=-\frac{(a+b)^2}{r}.\,e^{ik(ct-r+a+b)}\,\Sigma\,\frac{A_n\,P_n(\cos\theta)}{F_n(ik.\,\overline{a+b})}\,f_n(ikr).$$

Now when r is large,

$$f_n(ikr)=1,$$

so that the factor on which the relative intensities in various directions depend is

$$\Sigma\ A_n\ \frac{P_n(\cos\theta)}{F_n(ik.\,\overline{a+b})}.$$

Thus if we put this quantity $=F+iG$, the intensity of the vibrations in various directions is measured by F^2+G^2.

The distribution of intensities in different directions round the spheres will be influenced to a considerable extent by the value of the wave-length chosen If we take $k(a+b) = 2$, the wave-length is 3π inches and if we take $k(a+b) = 3$, the wave-length is 2π inches. From the expression (1) for the wave-motion produced by a single sphere undergoing an instantaneous change of velocity, it is seen that the wave-length to be chosen is of the same order as the circumference of the sphere. From this, it appears that for a system of two spheres whose radii are 1 inch and 2 inches respectively, the wave-length to be chosen should be some value intermediate between 2π and 4π, probably nearer 2π than 4π; for, in the actual case of impact, the smaller ball which would undergo by far the greater change in velocity would probably influence the character of the motion to a greater extent than the larger sphere. At the same time it must not be forgotten that the analogy between the case of impact and the case of periodic motion cannot be pushed very far, in as much as the fluid motion due to impact is undoubtedly of different character in different directions, and not throughout the same as in the periodic case.

Now taking $k(a+b) = 2$, we find (neglecting a constant factor) that

$$F = \cdot 0992\ P_1(\cos\theta) + \cdot 2840\ P_2(\cos\theta) - \cdot 03535\ P_3(\cos\theta) - \cdot 01461\ P_4(\cos\theta) + \text{etc.}$$

$$G = \cdot 0496\ P_1(\cos\theta) - \cdot 4040\ P_2(\cos\theta) - \cdot 01767\ P_3(\cos\theta) + \cdot 0315\ P_4(\cos\theta) + \text{etc.} \quad (11)$$

The values of F, G and F^2+G^2 for different directions have been calculated and are shown in the following table :—

TABLE I.

Angles (in degrees.)	F × const.	G × const.	(F^2+G^2) × (const.)
0	+ 329,000	− 338,000	223,144
10	+ 325,908	− 326,525	212,552
20	+ 297,435	− 273,545	162,738
30	+ 251,537	− 214,337	109,300
40	+ 189,095	− 114,659	48,946
50	+ 114,215	− 24,167	13,572
60	+ 33,341	+ 74,407	6,565
70	− 43,647	+ 155,306	25,961
80	− 107,073	+ 205,212	53,574
90	− 147,250	+ 213,625	67,405
100	− 158,815	+ 178,920	57,322
110	− 140,329	+ 106,238	30,836
120	− 95,149	+ 8,675	9,106
130	− 34,099	− 99,267	10,957
140	+ 35,677	− 202,159	42,100
150	+ 1,02,819	− 289,237	94,130
160	+ 157,865	− 353,605	150,280
170	+ 192,648	− 392,229	190,913
180	+ 201,000	− 404,000	203,617

Now taking $k(a+b)=3$, we find (neglecting a constant factor) that

$$F = \cdot105 P_1(\cos\theta) + 1\cdot06 P_2(\cos\theta) + \cdot016 P_3(\cos\theta) - \cdot281 P_4(\cos\theta) - \text{etc.}$$

$$G = -\cdot1225 P_1(\cos\theta) + \cdot186 P_3(\cos\theta) - \cdot024 P_4(\cos\theta) - \text{etc.} \quad (12)$$

The values in different directions have been calculated for these expressions and are shown in the following table :—

TABLE II.

Angles (in degrees.)	F × const.	G × const.	(F^2+G^2) × (const.)
0	+ 900,000	+ 38,000	811,444
10	+ 890,608	+ 28,804	794,265
20	+ 849,305	− 2,390	720,805
30	+ 752,167	− 45,754	567,620
40	+ 572,469	− 90,446	335,284
50	+ 309,902	− 123,998	111,476
60	− 5,783	− 135,346	18,261
70	− 313,014	− 118,446	111,893
80	− 542,728	− 73,554	300,178
90	− 635,375	− 9,000	403,306
100	− 571,364	+ 60,786	329,762
110	− 371,618	+ 118,638	154,545
120	− 96,799	+ 149,218	31,610

Angles (in degrees.)	F × const.	G × const.	(F^2+G^2) × (const.)
130	+ 184,472	+ 144,494	54592,
140	+ 412,409	+ 105,758	180,980
150	+ 559,907	+ 44,650	315,625
160	+ 630,625	— 21,410	398,607
170	+ 654,606	— 69,748	433,925
180	+ 658,000	— 88,000	440,708

The values of F^2+G^2 shown in Tables I and II have been plotted in polar co-ordinates in figs. 3 and 4. It is seen that in both cases, the intensity in the direction of the larger ball is greater than in the direction of the smaller ball. The asymmetry is most marked when $k(a+b)$ has the larger value.

The intensity of the sound in different directions due to the impact of two spheres of wood, diameters 3 inches and $1\frac{1}{2}$ inches respectively, has been measured with the ballistic phonometer and is shown in Fig. 5.

It is seen that the curve is intermediate in form between those shown in fig. 3 and fig. 4, exactly as anticipated. The agreement between theory and experiment is thus very striking in this case.

3. *Two spheres of the same diameter but of different materials.*

We have seen in the preceding section that in the expressions F and G for two spheres of the same material but of unequal diameters, the terms contain-

ing the second order zonal harmonic $P_2(\cos\theta)$ usually preponderate, and that the intensity diagram is accordingly a curve which consists of four loops. A different result is obtained in the case of two spheres of the same diameter but of markedly unequal densities. The zonal harmonic of the first order preponderates in this case and the intensity diagram is a curve consisting of only two loops. To obtain this result theoretically we have to proceed on exactly the same lines as in the preceding pages.

Taking $a = 1$ inch and $b = 1$ inch, we easily find from the expressions (7) and (8) that

$$\begin{aligned}
2\phi = &\left[1-\frac{1}{2^3}+\frac{1}{3^3}-\frac{1}{4^3}+\frac{1}{5^3}-\text{ etc.}\right]\frac{P_1(\cos\theta)}{r^2}\\
&+2\left[1-\frac{1}{2^4}+\frac{1}{3^4}-\frac{1}{4^4}+\frac{1}{5^4}-\text{ etc.}\right]\frac{P_2(\cos\theta)}{r^3}\\
&+3\left[1-\frac{1}{2^5}+\frac{1}{3^5}-\frac{1}{4^5}+\frac{1}{5^5}-\text{ etc.}\right]\frac{P_3(\cos\theta)}{r^4}\\
&+4\left[1-\frac{1}{2^6}+\frac{1}{3^6}-\frac{1}{4^6}+\frac{1}{5^6}-\text{ etc.}\right]\frac{P_4(\cos\theta)}{r^5}\\
&+\text{etc.}
\end{aligned}$$

$$\begin{aligned}
2\phi' = -&\left[1-\frac{1}{2^3}+\frac{1}{3^3}-\frac{1}{4^3}+\frac{1}{5^3}-\text{ etc.}\right]\frac{P_1(\cos\theta)}{r^2}\\
&+2\left[1-\frac{1}{2^4}+\frac{1}{3^4}-\frac{1}{4^4}+\frac{1}{5^4}-\text{ etc.}\right]\frac{P_2(\cos\theta)}{r^3}\\
&-3\left[1-\frac{1}{2^5}+\frac{1}{3^5}-\frac{1}{4^5}+\frac{1}{5^5}-\text{ etc.}\right]\frac{P_3(\cos\theta)}{r^4}\\
&+4\left[1-\frac{1}{2^6}+\frac{1}{3^6}-\frac{1}{4^6}+\frac{1}{5^6}-\text{ etc.}\right]\frac{P_4(\cos\theta)}{r^5}\\
&-\text{etc.}
\end{aligned} \tag{13}$$

Summing the series we easily find that the vibrations

$$\left[U_a\frac{\partial\phi}{\partial r}+U_b\frac{\partial\phi'}{\partial r}\right]_{r=2} e^{ikct}$$

on the surface of the enveloping sphere can be expressed in the form

$$\tfrac{1}{2}\Big[(U_a-U_b)\times{\cdot}2254\ P_1(\cos\theta)+(U_a+U_b)\times{\cdot}3550\ P_2(\cos\theta)$$
$$+(U_a-U_b)\times{\cdot}3645\ P_3(\cos\theta)+(U_a+U_b)\times{\cdot}3080\ P_4(\cos\theta)$$
$$+(U_a-U_b)\times{\cdot}2325\ P_5(\cos\theta)+\text{etc.}\Big]\,e^{ikct} \qquad (14)$$

If the ball of radius b is four times heavier than the one of radius a, we have

$$U_a=4\ U_b.$$

So that the vibrations on the surface of the enveloping sphere is proportional to the expression

$$\Big[{\cdot}6762\ P_1(\cos\theta)+1{\cdot}7750\ P_2(\cos\theta)+1{\cdot}0935\ P_3(\cos\theta)$$
$$+1{\cdot}5400\ P_4(\cos\theta)+{\cdot}6975\ P_5(\cos\theta)+\text{etc.}\Big]\,e^{ikct}$$

Now taking $k\,(a+b)=1$, which will give a wave-length equal to the circumference of the enveloping sphere, we get

$$F=\ {\cdot}13524\ P_1(\cos\theta)-{\cdot}04987\ P_2(\cos\theta)-{\cdot}0074\ P_3(\cos\theta)$$
$$+{\cdot}0007\ P_4(\cos\theta)+\text{etc.}$$

$$G=-{\cdot}0676\ P_1(\cos\theta)-{\cdot}0798\ P_2(\cos\theta)+{\cdot}0047\ P_3(\cos\theta)$$
$$+{\cdot}0012\ P_4(\cos\theta)-\text{etc.}$$

The values of F and G, and of F^2+G^2 in different directions obtained from the preceding expressions are shown in Table III.

TABLE III.

Angles (in degrees.)	F × const.	G × const.	$(F^2+G^2)\times$ (const.)
0	+ 786,000	− 1,415,000	2,620,021
10	+ 793,732	− 1,374,897	2,521,061
20	+ 813,819	− 1,256,037	2,240,132
30	+ 835,068	− 1,068,615	1,839,986
40	+ 845,629	− 826,059	1,397,992
50	+ 828,667	− 549,652	989,741
60	+ 768,690	− 262,257	660,005
70	+ 654,594	+ 7,901	427,780
80	+ 482,433	+ 237,049	288,493
90	+ 252,125	+ 403,500	225,913
100	+ 228,907	+ 495,515	297,466
110	− 331,298	+ 509,107	368,642
120	− 647,986	+ 454,821	626,929
130	− 954,405	+ 347,884	1,031,220
140	− 1,229,335	+ 211,923	1,555,385
150	− 1,458,496	+ 71,667	2,130,948
160	− 1,629,521	− 47,667	2,655,850
170	− 1,734,880	− 128,811	3,026,866
180	− 1,770,000	− 157,000	3,157,549

The values of (F^2+G^2) shown in Table III have been plotted in polar co-ordinates and are shown in fig. 6. It is seen that the maximum intensity in the direction of the heavier ball is greater than that in the direction of the lighter one.

The experimental curve of intensity of sound due to impact of a sphere of wood, diameter 2¼ inch, with a billiard ball of nearly the same size is shown in fig. 7. It is found that the directions of minimum intensity are not quite in the plane perpendicular to the line of impact, they being nearer the side of the lighter ball.

A result of some importance indicated by theory is that when one of the spheres is much heavier than the other, replacing the former by a still heavier sphere of the same diameter should not result in any important alteration in the distribution of the intensity of sound in different directions due to impact. This is clear from expression (14). For when U_a is much larger than U_b, any diminution in the value of U_b should not appreciably affect the value of the expression. This indication of theory is in agreement with experiment. Several series of measurements have been made with various pairs of balls of the same size but of different densities, namely, wood and marble, wood and iron, billiard ball and iron ball and so forth. Generally similar results are obtained in all cases. It was noticed also that the form of the intensity distribution as shown by the ballistic phonometer was not altogether independent of the thickness of the mica-disk used in the instrument. This is not surprising, as the behaviour of the mica-disk, before the pointer attached

to it ceases to touch the mirror of the indicator, would no doubt depend to some extent on the relation between its natural frequency and the frequency of the sound waves set up by impact. The best results have been obtained with a disk neither so thick as to be relatively insensitive, nor so thin as to remain with its pointer in contact with the indicator longer than absolutely necessary.

4. *The general case of spheres of any diameter and density.*

When the impinging spheres are both of different diameters and of different densities, the results generally obtained are that the sound is a maximum on the line of impact in either direction and a minimum which approaches zero in directions asymmetrically situated with reference thereto. Generally speaking no maxima in lateral derections are noticed, that is, the curve consists of two nearly closed loops. The difference of the intensity of the sound in the two directions of the line of impact may sometimes be considerable. As a typical case, the results obtained by the impact of a sphere of wood 3 inches in diameter with a brass sphere 1⅛ inches in diameter are shown in fig. 8. It is observed that the sound due to impact is actually of greater intensity on the side of the small brass ball. As a matter of fact the result generally obtained is that the intensity is greater on the side of the ball of the denser material, even if its diameter be smaller.

The mathematical treatment of the general case is precisely on the same lines as in the two preceding sections. It is found in agreement with the experimental result that in practically all cases in which both

the densities and the diameters are different, that the zonal harmonic of the first order is of importance and that the intensity curve consists of two nearly closed loops, as in the case of two spheres of the same diameter but of different densities.

5. *Summary and Conclusion.*

The investigation of the origin and character of the sound due to the direct impact of two similar solid spheres which was described in the Phil. Mag. for July, 1916, has been extended in the present paper to the cases in which the impinging spheres are not both of the same diameter or material. The relative intensities of the sound in different directions have been measured by the aid of the ballistic phonometer, and in order to exhibit the results in an effective manner, they have been plotted in polar co-ordinates, the point at which the spheres impinge being taken as the origin, and the line of collision as the axis of x. As might be expected, the curves thus drawn show marked asymmetry in respect of the plane perpendicular to the line of impact.

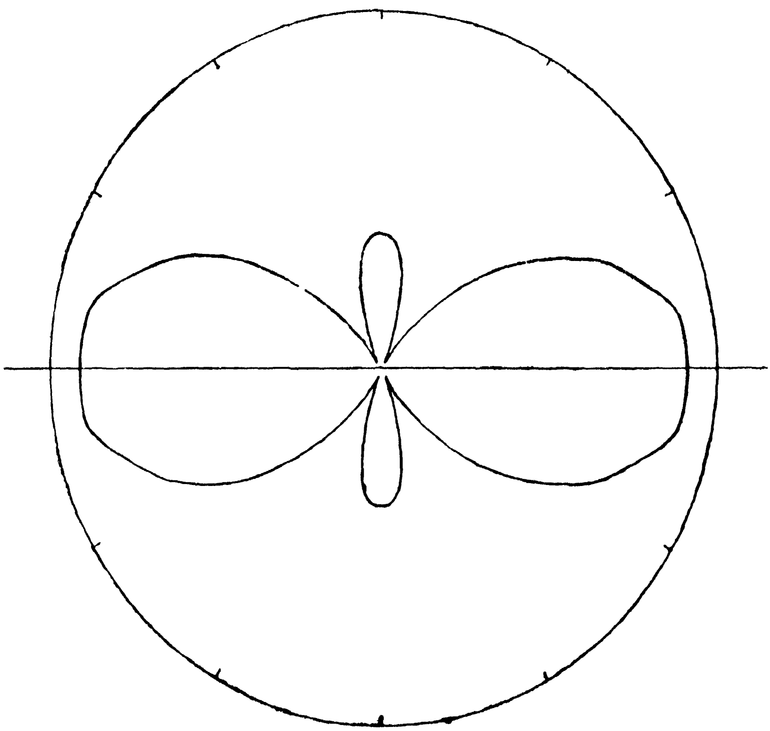
A detailed mathematical discussion of the nature of the results to be expected is possible by considering the analogous case of two rigid spheres nearly in contact which vibrate bodily along the line of centres. By choosing an appropriate wave-length for the resulting motion, intensity curves similar to those found experimentally for the case of impact are arrived at. A further confirmation is thus obtained of the hypothesis regarding the origin of the sound suggested by the work of Hertz and of Lord Rayleigh on the theory of elastic impact.

When the impinging spheres, though not equal in size, are of the same or nearly the same density, the intensity curve drawn for the plane of observation shows the sound to be a maximum along the line of impact in either direction, and also along two directions making equal acute angles with this line. The sound is a minimum along four directions in the plane.

In practically all other cases, that is when the spheres differ considerably either in density alone, or both in diameter and density, the intensity is found to be a maximum along the line of impact in either direction, and to be a minimum along directions which are nearly but not quite perpendicular to the line of impact. The form of the intensity curve is practically determined by the diameters and the masses of the spheres.

The investigation was carried out in the Physical Laboratory of the Indian Association for the Cultivation of science. It is hoped when a suitable opportunity arrives to study also the case of oblique impact. The writer has much pleasure in acknowledging the helpful interest taken by Prof. C. V. Raman in the progress of the work described in the present paper.

CALCUTTA,
The 15th of June, 1917.



Fig, 1.

Observed distribution of sound intensity around two equal colliding spheres of the same material.

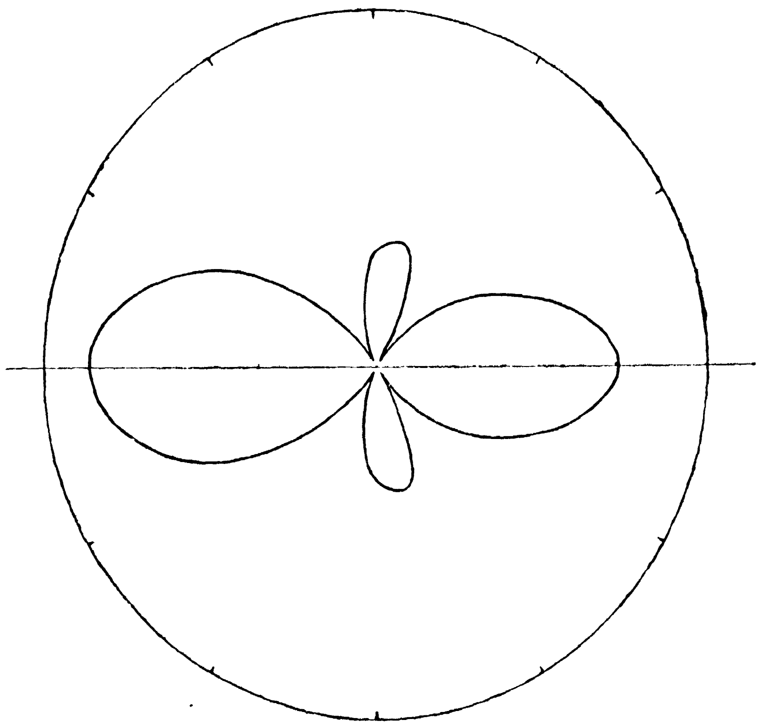


Fig. 2.

Observed distribution of intensity due to impact of two unequal spheres of wood.

Sphere on left ; 3 inches diameter.

Sphere on right ; $2\frac{1}{4}$ inches diameter.

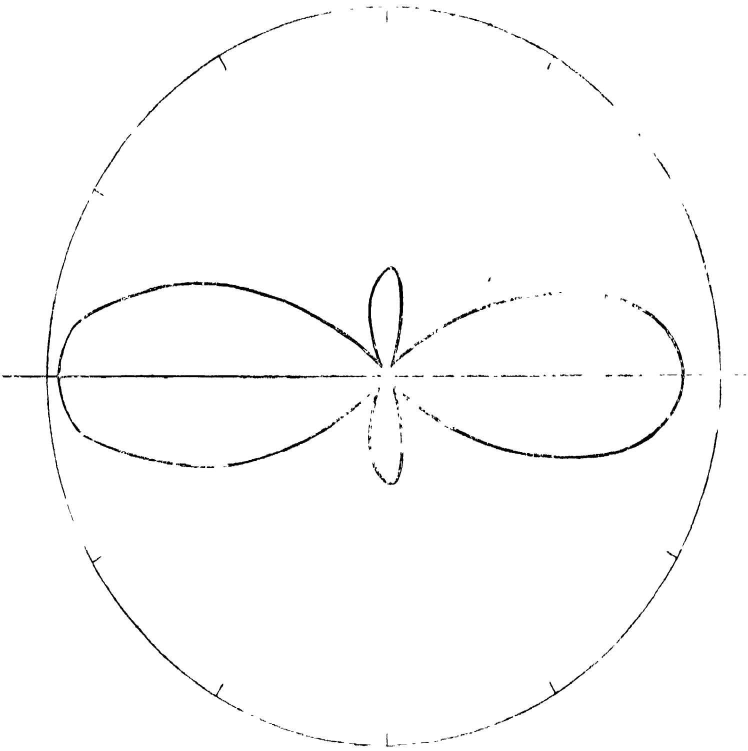


Fig. 3.

Calculated Form of Intensity Curve due to two Spheres of diameters 2 : 1. [$k(a+b)=2.$]

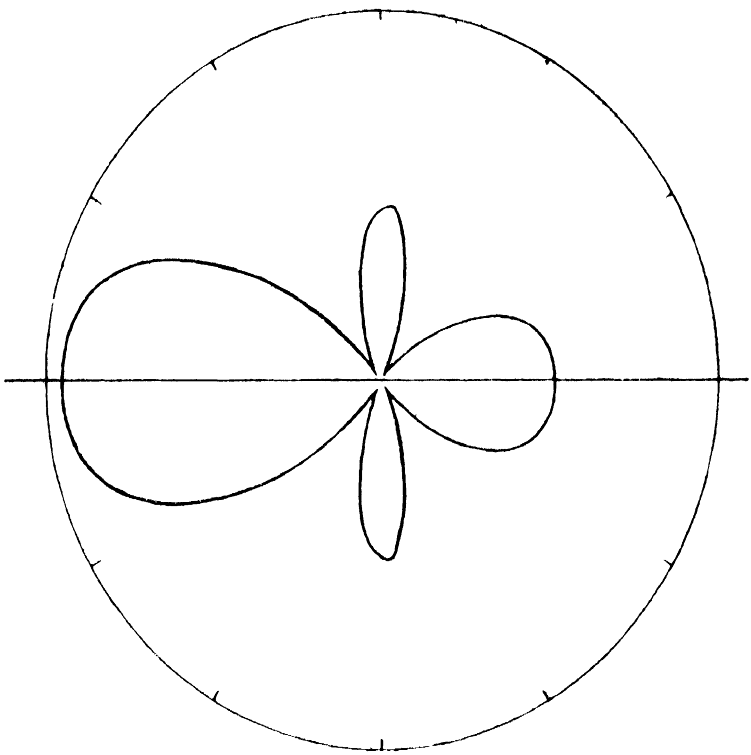


Fig. 4.

Same as fig. 3, but with $k(a+b)=3$.

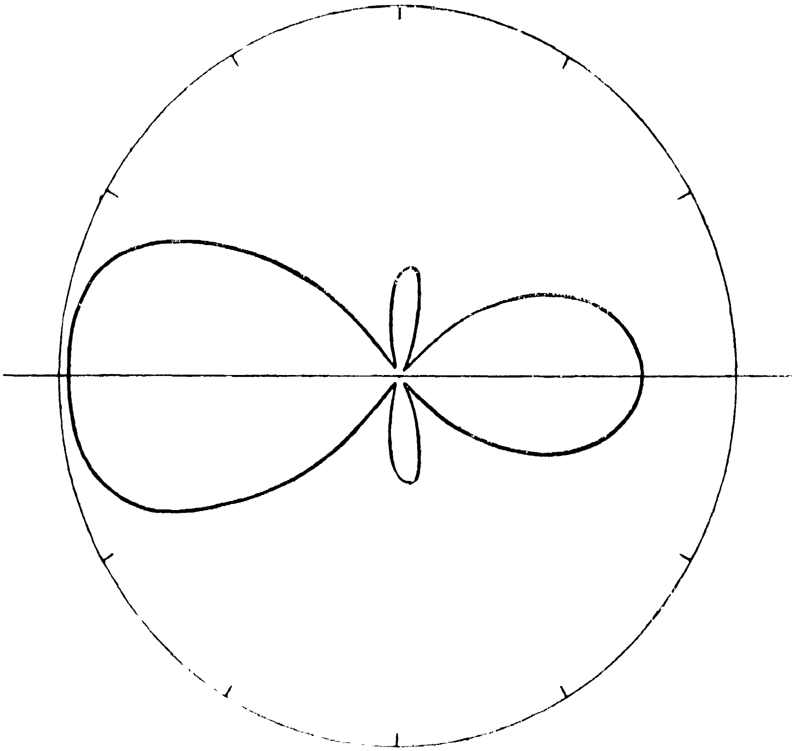


Fig. 5.

Observed Form of Intensity Curve due to impact of Spheres of diameters 2 : 1.

(Material, wood ; diameters 3 inches and $1\frac{1}{2}$ inches respectively).

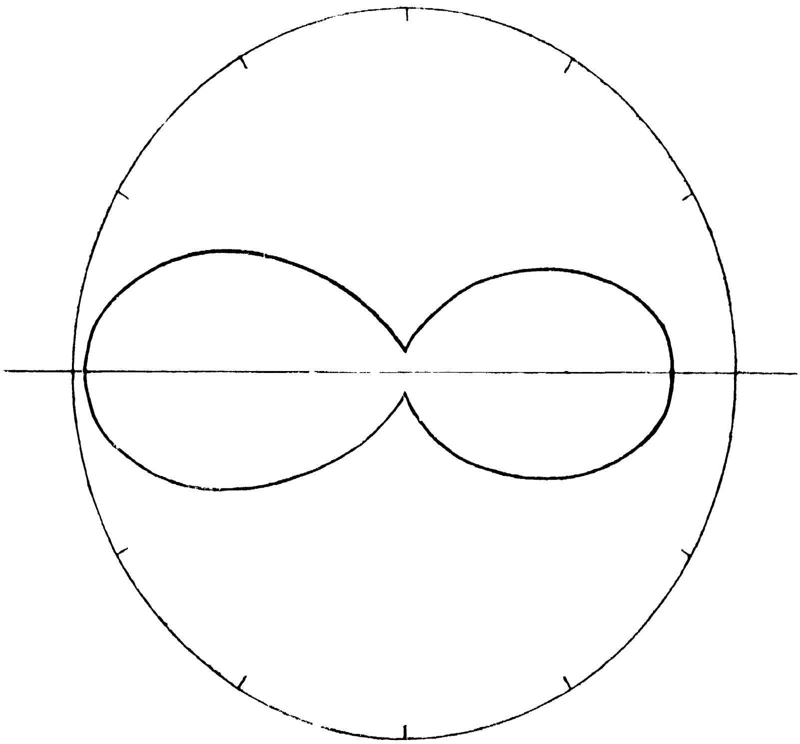


Fig. 6.

Calculated Form of Intensity Curve due to two equal Spheres of densities 4 : 1.

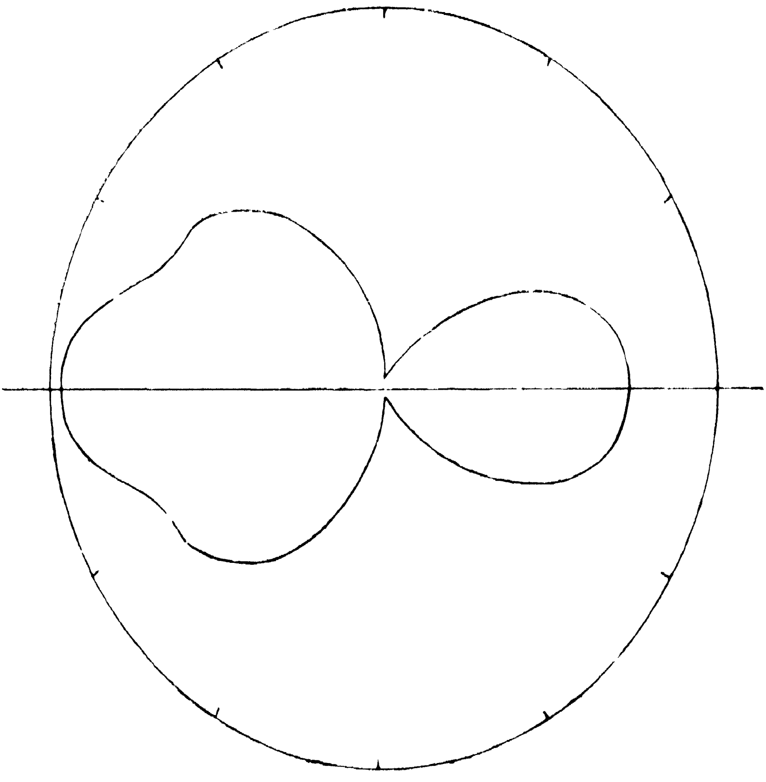


Fig. 7.

Observed Form of Intensity Curve due to impact of Spheres of nearly equal diameters but different materials

Sphere on left :	Sphere on right :
Material, billiard ball ;	Material, wood ;
Diameter, $2\frac{1}{8}$ inches,	Diameter, $2\frac{1}{4}$ inches ;
Mass, 150 gms.	Mass, 66 gms.

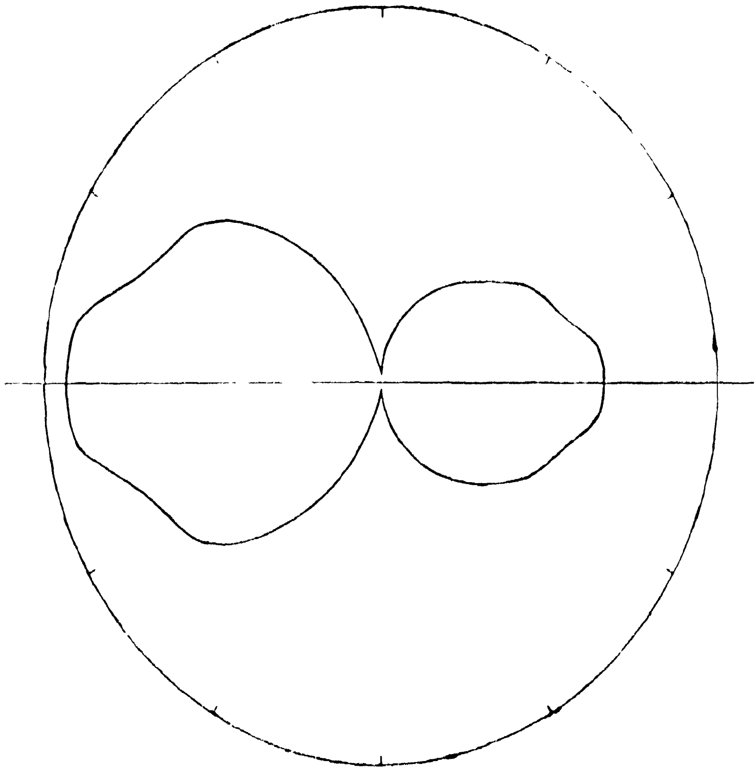


Fig. 8.

Observed Form of Intensity Curve due to impact of two Spheres of different diameters and densities.

Sphere on left:
Material, brass;
Diameter, $1\frac{1}{8}$ inches;
Mass, 118 gms.

Sphere on right:
Material, wood;
Diameter, 3 inches;
Mass, 158 gms.

PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

Vol. III. PART III.

On the Diffraction of Light by Cylinders of large Radius.

BY NALINIMOHAN BASU, M.Sc.

Introduction,

1. C. F. BRUSH has recently published a paper containing some interesting observations on the diffraction of light by the edge of a cylindrical obstacle*. Brush worked with cylinders of various radii (the finer ones being screened on one side so as to confine diffraction to the other side only), and observing the fringes formed within a few millimetres of the diffracting edge through a microscope, found that they appeared brighter and sharper with every increase in the radius of the cylinder. The fringes obtained with a smooth rod of one or two centimetres radius differed very markedly from these formed by a sharp edge or by a cylinder of small radius. They were brighter, more numerous, showed greater contrast between the maxima and minima of illumination, and their spacing was different from that given

* "*Some Diffraction Phenomena: Superposed Fringes*" by C. F. Brush, *Proceedings of the American Philosophical Society*, 1913, pages 276-282. See also *Science Abstracts* No. 1810 (1913).

by the usual Fresnel formulæ. Brush also observed that when the radius of the cylinder was a millimetre or more, the fringes did not vanish when the focal plane of the microscope was put forward so as to coincide with the edge of the cylinder. Sharp narrow fringes were observed with the focal plane in this position, becoming broader and more numerous as the radius of the cylinder was increased.

2. To account for these phenomena Brush has suggested an explanation, the nature of which is indicated by the title of his paper. The diffraction-pattern formed by the cylinder is, according to Brush, the result of the superposition of a number of diffraction-patterns which are almost, but not quite, in register. He regards the cylindrical diffracting surface as consisting of a great many parallel elements, each of which acts as a diffracting edge and produces its own fringe-pattern which is superposed on those of the other elements. Brush has made no attempt to arrive mathematically or empirically, at any quantitative laws of the phenomena described in his paper. A careful examination of the subject shows that the view put forward by him presents serious difficulties and is open to objection. One of the defects of the treatment suggested by Brush is that it entirely ignores the part played by the light regularly reflected from the surface of the obstacle at oblique or nearly grazing incidences. I propose in the present paper (*a*) to describe the observed effects in some detail, drawing attention to some interesting features overlooked by Brush, (*b*) to show that they can be interpreted in a manner entirely different from

that suggested by him, and (*c*) to give a mathematical theory together with the results of a quantitative experimental test.

3. Reference should be made here to the problem of the diffraction of plane electro-magnetic waves by a cylinder with its axis parallel to the incident waves. The solution of this problem for a perfectly conducting cylinder has been given by J. J. Thomson*, and for a dielectric cylinder by Lord Rayleigh†. These solutions are however suitable for numerical computation only when the radius of the cylinder is comparable with the wave-length. A treatment of the problem in the case of a cylinder of any radius has recently been given by Debye‡ He considers the electromagnetic field round a perfectly reflecting cylinder, whose axis is taken for the axis of z, with polar co-ordinates r, ϕ, and waves in the plane of xy polarised in the direction of z, the electric component in z being e^{ikx}. Expressing the disturbance-field in the form.

$$Z = -\Sigma e^{in\frac{\pi}{2}} \cdot \frac{J_n(ka)}{H_n(ka)} \cdot H_n(kr) \cos n\phi$$

(in which J_n is the usual Bessel function, H_n is Hankel's second cylindrical function and $k = \frac{2\pi}{\lambda}$), Debye

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* "*Recent Researches in Electricity and Magnetism*", p. 428.

† *Phil Mag*, 1881. Scientific works, Vol. 1, p. 584.

‡ P. Debye, "*On the Electromagnetic field surrounding a Cylinder and the theory of the Rainbow*", *Phys. Zeitscher.* 9. pp. 775-778, Oct., 1908, and *Science Abstracts*, No. 258, 1909.

transforms the solution into the simple form

$$Z = -\sqrt{\frac{a \cos\frac{\phi}{2}}{2r}} \cdot e^{-ik\left(r - 2a\cos\frac{\phi}{2}\right)}.$$

Debye's work is of considerable significance but his final result is valid only for points at a great distance from the surface of the cylinder, whereas the phenomena considered in the present paper are those observed in its immediate neighbourhood. No complete mathematical treatment of the subject now dealt with appears to have been given so far.

General Description of the Phenomena.

4. The experimental arrangements adopted are those shewn in the diagram (fig. 1.).

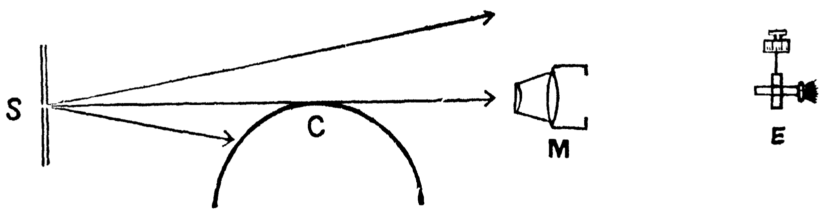


Fig. I.

Light from a slit S falls on a polished cylinder of metal or glass and passes it tangentially at C*. The axis of the cylinder is parallel to the slit. A collimating lens may, if necessary, be interposed between the slit and cylinder. The fringes bordering the shadow of the edge C are observed through the miscroscope-objective M and the micrometer eyepiece E. The latter may be placed at any convenient distance from

* A glass cylinder may be used without inconvenience as the light transmitted through the cylinder is refracted out to one side and does not enter into the field under observation. Very little light is, in fact, transmitted through the cylinder at oblique incidences.

the objective so as to give the necessary magnification. The effects are best seen with monochromatic light which may be obtained by focussing the spectrum of the electric arc on the slit with a small direct-vision prism. For photographic work, the eyepiece E is replaced by a long light-tight box in front of which the objective is fixed, and at the other end of which the photographic plate is exposed. Sufficient illumination for photographing the fringes may be secured by using the arc and illuminating the slit by the greenish-yellow light transmitted by a mixture of solutions of copper sulphate and potassium bichromate.

5. The phenomena observed depend on the position of the focal plane of the objective with reference to the diffracting edge of the cylinder, and an interesting sequence of changes is observed as the focal plane of the objective is gradually moved towards the light, up to and beyond the edge C (fig. 1) at which the incident light grazes the cylinder. Some idea of these changes will be obtained on a reference to Plate I, figs. I to VIII, in which the fringes photographed with a cylinder of radius 1·54 cm. are reproduced. (A Zeiss objective of focal length 1·7 cm. was used and the magnification on the original negative was 135 diameters.)

6. To interpret the phenomena it is convenient to compare them with those obtained when the cylinder is replaced by a sharp diffracting edge in the same position. Using the cylinder, it is found that when the focal plane is between objective and the cylinder, but several centimetres distant from the

latter, the fringes are practically of the same type as those due to a sharp diffracting edge. They are diffuse, few in number (not more than seven or eight being visible even in monochromatic light), and the first bright band is considerably broader and more luminous than the rest. The fringes become narrower (retaining their characteristics) as the focal plane is brought nearer the cylinder till the distance between the two is about two centimetres. At this stage some new features appear; the contrast between the minima and maxima of illumination becomes greater than in the fringes of the usual Fresnel type, and the number that can be seen and counted in monochromatic light increases considerably. These features become more and more marked as the focal plane approaches the cylinder, and the dark bands then become almost perfectly black. The difference between the intensity of the first maximum and of those following it also becomes less conspicuous. Figs. I., II., and III. in the Plate represent these stages. A considerable brightening-up of the whole field is also noticed as focal plane approaches the cylinder, but this is not shown in the photographs, as the exposures obtained with the light of the arc were very variable. When the focal plane is within a millimetre or two of the edge at which the incident light grazes the cylinder, a change in the law of spacing of the fringes also becomes evident, the widths of successive bright bands decreasing less rapidly than in the fringes of of the Fresnel type. Fig. IV. in the plate illustrates this feature, which is most marked when the focal plane coincides with the edge of the cylinder. At

this stage, of course, the fringes due to a sharp diffracting edge would vanish altogether.

7. When the focal plane is gradually moved further in, so that it lies between the cylinder and the source of light, some very interesting effects are observed. The fringes contract a little, and the first band, instead of remaining in the fixed position defined by the geometrical edge, moves into the region of the shadow, and is followed by a new system of fringes, characterized by intensely dark minima, that appears to emerge from the field occupied by the fringes seen in the previous stage. (See figs. V. and VI.) The first band of this new system is considerably more brilliant than those that follow it. It is evident on careful inspection that the fringes that move into the shadow form an independent system. For it is found that the part of the field from which the new system has separated out appears greatly reduced in intensity in comparison with the part on which it is still superimposed. When the separation of the field into two parts is complete, a few diffraction-fringes of the usual Fresnel type are observed at the geometrical edge of the shadow of the cylinder. (See figs. VII. and VIII. in the Plate, in which this position is indicated by an arrow.)

8. A comparison of the effects described in the preceding paragraph and of those obtained with a sharp diffracting edge in the same position, furnishes the clue to the correct explanation of the phenomena observed and dealt with in the present paper. With a sharp edge, the fringes of the Fresnel type disap-

pear when the focal plane coincides with it, and reappear without alteration of type when the focal plane is between the edge and the source of light. As already remarked and shown in Plate I, figs. VII and VIII, fringes of this type may also be observed with the cylinder when the focal plane is in this position, and in addition we have inside the shadow an entirely separate system of fringes characterised by perfectly black minima and a series of maxima with intensities converging to zero. This latter system has nothing in common with the diffraction phenomena of the Fresnel class and has obviously an entirely different origin. That it is formed exclusively by the light reflected from the surface of the cylinder is proved by the fact that it may be cut off without affecting the rest of the field by screening the surface of the cylinder. It is accordingly clear that the light reflected from the surface of the cylinder plays a most important part in the explanation of the phenomena, and that the edge of the cylinder grazed by the incident rays alone acts as a diffracting edge in the usual way, and not all the elements of the surface as supposed by Brush. We shall accordingly proceed on this basis to consider the theory of the fringes observed in various positions of the focal plane.

Theory of the Fringes at the edge of the Cylinder.

9. When the focal plane coincides with the edge at which the incident light grazes the cylinder, it is permissible to regard the fringes seen as formed by simple interference between the light that passes the cylinder unobstructed and the light that suffers re-

flection at the surface of the cylinder at various incidences. For if a sharp diffracting edge were put in the focal plane, no diffraction fringes would be visible. The positions of the minima in the field may be readily calculated.

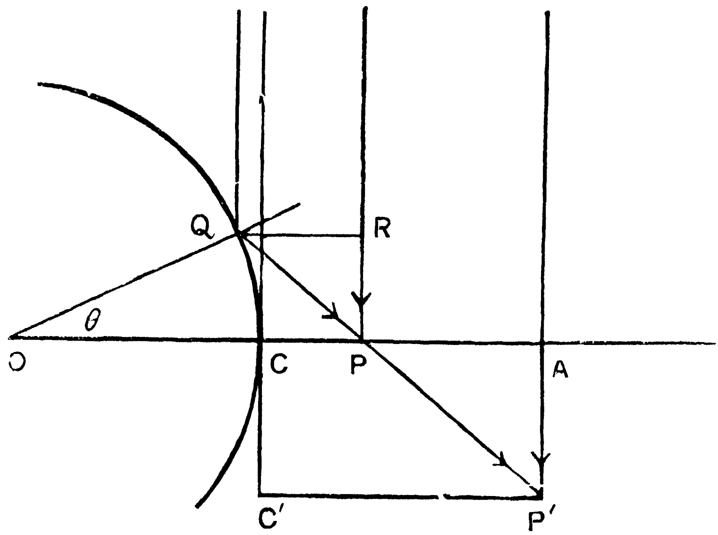


Fig. 2.

In fig. 2, let O be the centre of the cross-section of the cylinder in the plane of incidence, and let C be the point at which the incident light grazes the cylinder. It is sufficient for practical purposes to consider the incident beam as a parallel pencil of rays. The ray meeting the cylinder at the point Q is reflected in the direction Q P. Let the angle $QOA=\theta$, so that the angle $OQP=\frac{\pi}{2}+\theta$, and the angle $OPQ=\frac{\pi}{2}-2\theta$. Let a be the radius of the cylinder and $CP=x$. The difference of path, δ, between the direct ray and the reflected ray reaching the point P is evidently equal to $QP-RP$ which can be easily shewn to be given by

$$\delta=a\sin\theta\,(\sec 2\theta-1).$$

Similarly we shall have

$$x = a \sec 2\theta\ (\cos\theta - \cos 2\theta).$$

Therefore, neglecting 4th and higher powers of θ, we have

$$\delta = a\theta^3, \text{ and } x = 3a\theta^2/2,$$

so that $\delta = 2a\left(\frac{2x}{3a}\right)^{\frac{3}{2}}$.

Since the rays suffer a phase-change of half a wave-length by reflexion, the edge C will from the centre of a dark band and the successive minima are therefore given by

$$x = \frac{3a}{2}\cdot\left(\frac{n\ \lambda}{2a}\right)^{\frac{2}{3}} = \tfrac{3}{4}\cdot\ (2a)^{\frac{1}{3}}.\ (n\ \lambda)^{\frac{2}{3}},$$

where $n = 1, 2, 3$, etc The results calculated according to the above theory and those found in experiment are given in Table I.

TABLE I.

Widths of bright bands in cm.

$a = 1{\cdot}54$ cm, $\lambda = 6562 \times 10^{-8}$ cm.

n	Observed widths.	Calculated widths.
1	0·00174	0·001775
2	0·00102	0·001019
3	0·00086	0·000875
4	0 00076	0·000781
5	0·00069	0·000717
6	0·00068	0·000671

The discrepancies are within the limits of experimental error. When making these measurements, the focal plane was in the first instance set in ap-

proximate coincidence with edge of the cylinder by noting the stage at which a further movement of the focal plane towards the light results in a movement of the fringes into the region of the shadow. There was however a slight uncertainty in regard to this adjustment and the best position of the focal plane was finally ascertained by actual trial.

10. The ratio between the maxima and minima of illumination in the fringes at the edge of the cylinder may readily be calculated. Dividing up the pencil of rays incident on the cylinder into elements of width $a \sin \theta . d\theta$, or $a\theta . d\theta$ approximately, the width of the corresponding elements of the reflected pencil in the plane of the edge is, dx, that is, $3a\theta\, d\theta$. The amplitude of the disturbance at any point in this plane due to the reflected rays, is thus only $1/\sqrt{3}$ of that due to the direct rays, multiplied by the reflecting power of the surface. If the reflecting power be unity (as is practically the case at such oblique incidences), the ratio of the intensities of the maxima and minima is $(1 + 1/\sqrt{3})^2 : (1 - 1/\sqrt{3})^2$, that is approximately 14:1. The dark bands are thus nearly, but not quite, perfectly black.

Theory of the Fringes at the Edge of the Shadow.

11. If the fringes be observed in a plane (such as C′P′ in fig. 2) which is farther from the source of light than the edge of the cylinder, the diffraction and mutual interference of the direct and the reflected rays have both to be taken into account. Since the reflected rays from a divergent pencil while the incident rays are parallel, the effect of the former at any

point sufficiently remote from the cylinder would be negligible in comparison with the effect of the latter. If d, the distance of the plane of observation from the edge of the cylinder, be sufficiently large, the problem thus reduces to one of simple diffraction of the incident waves by the straight edge C. The position of the minima of illumination with reference to the geometrical edge of the shadow would then be given approximately by the simple formula

$$x' = \sqrt{2nd\lambda} = \sqrt{d\lambda/2}\sqrt{4n}$$

where $x' = C'P'$, and $d = C\ C'$

or with great accuracy by Schuster's formula

$$x' = \sqrt{(8n-1)d\lambda/4} = \sqrt{d\lambda/2}.\sqrt{(8n-1)/2}$$

These two formulæ give results which do not differ materially except in regard to the first two or three bands as can be seen from Table II.

TABLE II.

(1) n	(2) $\sqrt{4n}$	(3) $\sqrt{(8n-1)/2}$	(4) Proportionate widths of bands as per column (2)	(5) Proportionate widths of bands as per column (3)
1	2·000	1·871	2·000	1·871
2	2 828	2·739	0 828	0 868
3	3·464	3·391	0 636	0 652
4	4·000	3·937	0·536	0 546
5	4·472	4·416	0·472	0·479
6	4·899	4·848	0·427	0·432
7	5·292	5·244	0·393	0·396

12. If d be not large, the intensity of the reflected rays is not negligible. The following considerations enable us to find a simple formula for the position of the minima of illumination which takes both diffraction and interference into account. We may, to begin with, find the positions of the minima assuming the case to be one of simple interference between the direct and the reflected rays. The expression for the path difference, δ', of the rays arriving at the point P' is readily seen from fig. 2 to be given by the formulæ

$$\delta' = (d + e \sin \theta)\ (\sec 2\theta - 1).$$
$$\text{and } x' = d \tan 2\theta + a\ (\cos \theta \sec 2\theta - 1).$$

These two relations may: to a close approximation, be written in the form

$$\delta' = 2d\theta^2 + 2a\theta^3.$$
$$\text{and } x' = 2d\theta + 3a\theta^3/2,$$

Putting $d=o$, we get the formula already deducted (see paragraph 9 above) for the fringes at the edge C of the cylinder. On the other hand if d be greater than a, we may, to a sufficient approximation, write

$$\delta' = 2d\theta^2 \text{ and } x' = 2d\theta,$$

and the positions of the points at which the direct and the reflected rays are in opposite phases are given by the formula

$$z' = \sqrt{2nd\lambda}$$

13. But, as remarked above, the simple formula $x' = \sqrt{2nd\lambda}$ also gives the approximate positions of the minima in the diffraction-fringes at a considerable distance from the cylinder where the effect of the reflected rays is negligible. It is thus seen that the formulæ

$$\left.\begin{array}{l} n\lambda = 2d\theta^2 + 2a\theta^3, \\ \text{and } \quad x' = 2d\theta + 3a\theta^3/2, \end{array}\right\} \quad \cdots \qquad \cdots \quad \text{(A)}$$

suffice to give the approximate positions of the minima of illumination at the edge of the cylinder (at which point the fringes are due to simple interference of the direct and the reflected rays) and also at a considerable distance from it (in which case they are due only to the diffraction of the incident light) *A priori* therefore, it would seem probable that the formulæ would hold good also at intermediate points, that is for all values of d. That this is the result actually to be expected may be shown by considering the effect due to the reflected rays at various points in in the plane of observation. The reflected wave-front is the involute of the virtual caustic (see fig. 3 below). At the edge C, the radius of curvature of the wave-front is zero, and increases rapidly as we move outwards from the edge of the cylinder. The reflected rays accordingly suffer the most rapid attenuation due to divergence in the direction of the incident rays, and less rapid attenuation in other directions. In any plane C′P′, therefore, the effect of the reflected light is negligible in the immediate neighbourhood of the point C′, and would be most perceptible at points farthest removed from C′.* On the other hand, the fluctuations of intensity due to the diffraction of the direct rays are most marked in the neighbourhood of C′, that is, for the smallest values of θ. We should accordingly expect to find that when d is not zero, the first few bands are practically identical in position with those due to simple diffraction, and those following are due to simple interference bet-

* Debye's formula (*loc. cit.*) shows that the intensity of the reflected light becomes very small as ϕ approaches π.

ween the direct and the reflected rays. The formulæ given above satisfy both of these requirements. For it is obvious from the manner in which they have been deduced that they satisfy the second requirement. The first requirement is also satisfied, as, by putting θ small, the formulæ reduce to $n\lambda = 2d\theta^2$ and $x' = 2d\theta$; or, in other words, $x' = \sqrt{2nd\lambda}$, for the minima of illumination, which is also the usual approximate diffraction formula. Accordingly, the complete formulæ $n\lambda = 2d\theta^2 + 2a\theta^3$ and $x' = 2d\theta + 3a\theta^2/2$ would (on eliminating θ) give the positions of the minima over the entire field with considerable accuracy.

14. The statements made in the preceding paragraph are, however, subject to an important qualification. The validity of the formula obtained rests on the basis that, for large values of *d*, the positions of the minima of illumination are given by the simple relation $x' = \sqrt{2nd\lambda}$. This, however, is only an approximation, as the accurate values are to be found from Schuster's formula (see Table II), when the reflected light is negligible When *d* is so large that the formulæ $n\lambda = 2d\theta^2 + 2a\theta^3$ and $x' = 2d\theta + 3a\theta^2/2$ give nearly the same positions for the minima as the simple relation $x' = \sqrt{2nd\lambda}$, they should therefore cease to be strictly valid. The actual positions of the minima for such values of *d* should agree more closely with those given by Schuster's formula, and should, when *d* is very large, agree absolutely with the same. This qualification is, however, of importance only with reference to the first two or three bands obtained for fairly large values

of d. The differences in respect of the other bands would be negligibly small.

15. To test the foregoing results measurements were made of the widths of the bright bands for a series of values of d up to 2 cms. Table III shows the observed values, the values calculated from my formula, and the values according to Schuster's formula (which would be valid for a sharp diffracting edge in the same position). To calculate the positions of the minima given by the relations $n\lambda = 2d\theta^2 + 2a\theta^3$, and $x' = 2d\theta + 3a\theta^2/2$, the first equation was solved for θ by Horner's method and the resulting values substituted in the second equation. The measurements of the width of the first band were rather rough on account of the indefiniteness of its outer edge. The agreement between the observed widths and the widths calculated from my formulæ is seen to be fairly satisfactory for values of d up to 3 mms. For larger values of d, the observed widths agree more closely with those calculated from Schuster's formula as explained in paragraphs 11 and 14 above.

TABLE III.

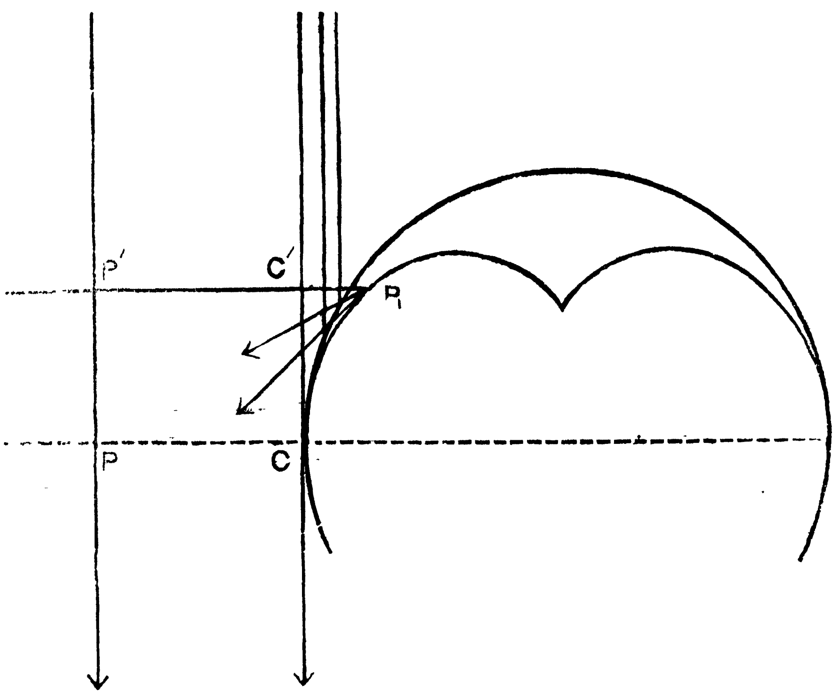
Widths of bright bands in cm. $\times 10^{-5}$.

$a = 1{\cdot}54$ cm. $\lambda = 6562 \times 10^{-8}$ cm.

n	Observed values.	Calculated [Formula (A)]	Calculated [Schuster's formula.]	Observed values.	Calculated [Formula (A)]	Calculated [Schuster's formula.]	Observed values.	Calculated [Formula (A).]	Calculated [Schuster's formula]
	$d = {\cdot}5$ mm.			$d = 1$ mm.			$d = 1{\cdot}5$ mm.		
1	277	291	239	397	385	339	471	458	415
2	133	140	111	173	170	157	198	199	193
3	107	111	83	134	134	118	154	155	145
4	95	98	70	119	116	99	133	133	121
5	86	89	61	100′	103	87	114	119	106
6	80	81	55	93	97	78	106	110	96
	$d = 2$ mm.			$d = 2{\cdot}5$ mm.			$d - 3$ mm.		
1	527	522	479	594	578	536	606	636	587
2	224	225	222	256	247	249	274	273	272
3	173	175	167	194	197	187	211	201	202
4	141	146	140	161	160	156	179	178	174
5	131	133	123	138	145	137	153	154	150
6	108	121	115	129	129	124	141	141	136
	$d = 5$ mm.			$d = 10$ mm.			$d \times 20$ mm.		
2	349	340	351	486	477	497	699	672	703
3	267	263	264	375	366	373	514	516	528
4	223	223	221	315	308	313	442	435	442

Theory of the Fringes between the edge and the source of light.

16. As already remarked in paragraph 7, the direct and the reflected pencils tend to separate into distinct parts of the field when the focal plane of the observing microscope is put forward so as to lie between the edge of the cylinder and the source of light. Why this is so will be readily understood on a reference to fig. 3. The rays reflected from the surface



when produced backwards would touch the enveloping surface which lies within the cylinder. This surface which is virtually the caustic of the reflected rays terminates at the edge C of the cylinder, and when the focal plane of the observing microscope is moved forward from CP to a position P'C'P_1 in front

of the edge, the boundary of the field on the right-hand side would shift into the region of the shadow and would, in fact, lie on the surface of the caustic at the point P_1. If the plane $P'C'P_1$ is considerably forward of PC, the field is seen divided into two parts. The first part $P'C'$ consists of the direct rays alone (the reflected rays meetin $P'C'$ being too oblique to enter into the field of the observing microscope) and should obviously be bounded at C' by a few diffraction-fringes of the ordinary Fresnel type. The second part of the field P_1C' is due to the reflected rays alone and requires separate consideration.

17. In the case considered above, that is, when the focal plane is considerably in advance of the edge, the fringe-system within the shadow due to the reflected light is of the same type as that found by Airy in his well-known investigation on the intensity of light in the neighbourhood of a caustic. For the elementary pencils into which the reflected rays may be divided up diverge from points lying along the caustic, and if the point P_1 at which the focal plane intersects the caustic is sufficiently removed from the edge C at which the latter terminates, Airy's investigation becomes fully applicable, but not otherwise. The rays emerging from the point P_1 after passage through the objective of the microscope becomes a paralled pencil, while pencils emerging from points of either side of P_1 become convergent and divergent respectively. The reflected wave-front after passage through the objective has thus a point of inflexion, on either side of which it may be taken to extend indefinitely provided the are CP_1 be long

enough. Assuming the focal length to be f, and the equation of the wave front to be $\xi = A\eta^3$, the value of A may be readily found. The equation of the caustic is

$$(4x^2 + 4y^2 - a^2)^3 - 27a^4x^2 = 0.$$

From this, or directly by an approximate treatment, it may easily be shewn that the radius of curvature of the caustic at the point C is 3/4 of the radius of the cylinder. For our present purpose it is thus sufficient to treat the caustic as equivalent to a cylinder of radius $3a/4$ touching the given cylinder at C. We have

$$A = \tfrac{1}{6}\frac{d^3\xi}{d\eta^3} = \tfrac{1}{6}\frac{d}{d\eta}\left(\frac{d^2\xi}{d\eta^2}\right),$$

where $\frac{d^2\xi}{d\eta^2}$ is the measure of the convergence or divergence of the normals to the wave-front in the neighbourhood of the point of inflxion. Substituting the values obtained from the formulæ of geometrical optics, it is found that

$$A = \tfrac{1}{6}\,\frac{3a}{4}.\frac{1}{f^3} = \frac{a}{8f^3}.$$

The equation to the wave-front accordingly is

$$\xi = \frac{a}{8f^3}.\ \eta^3.$$

The illumination in the fringe-system is then given by Airy's formula

$$\mathrm{I} = 4\left[\int_0^\infty \cos\ \frac{\pi}{2}(\omega^3 + m\omega)\ d\omega\right]^2,$$

where $m = 4.2^{\frac{1}{3}}.a^{-\frac{1}{3}}.\lambda^{-\frac{2}{3}}.\ x_1,$

x_1 being the distance of any point in the focal plane measured from the point of intersection with the caustic, The integral gives a series of maxima of which the

first is the most intense, and the rest gradually converge to zero. The minima of illumination are zeroes.* As the focal plane is moved further and further towards the source of light, the fringe-system moves inwards along the caustic but remains otherwise unaltered.

18. The foregoing treatment of the reflected fringe-system in terms of Airy's theory ceases to be valid when the focal plane is not sufficiently in advance of the edge, and the arc CP_1 of the caustic is therefore not large enough. For the reflected wave-front on one side of the point of inflexion then becomes limited in extent and its equation cannot with sufficient accuracy be assumed to be of the simple from $\xi = A\eta^3$. In fact when the focal plane is at the edge of the cylinder, and CP_1 is zero, the point of inflexion on the reflected wave-front coincides with the edge, and is its extreme limit. At this stage, of course, the fringes seen in the field are due only to the interference of the direct and the reflected wave-trains. the phenomena noticed as the focal plane is advanced towards the source of light, represent a gradual transition from this stage to one in which Airy's theory becomes fully applicable. In the transition-stages the field of illumination is a continuous whole of which however the different parts present distinct characteristics. First, within the geometrical shadow of the edge we have a finite number of fringes (one, two or more according to the position of the plane of observation, but not an

* Graphs of Airy's integral and reference to the literature will be found in an interesting paper by Aichi and Tanakadate (*Journal of the College of Science*, Tokyo, vol. xxi. Art. 3).

indefinitely large number as contempled by Airy's theory); these may be regarded as the interference-fringes in the neighbourhood of the caustic due to the reflected light alone. Following these we have a long train of fringes due to the interference of the direct and the reflected pencils. The first few of these should evidently be modified by the diffraction which the direct rays suffer at the edge C before they reach the observing microscope. Finally, we may also have a part of the field in which the illumination is due only to the direct pencil, the reflected rays not entering the objective of the microscope owing to their obliquity. This part of the field should appear less brightly illuminated than the rest.

19. A complete theoretical treatment of the transition-stages described in the preceding paragraph is somewhat difficult, and has to be deferred to some future occasion. There is no difficulty, however, in calculating the positions of the fringes due to the inter-rerence of the direct and the reflected pencils when the focal plane is in advance of the edge, provided the diffraction-effect due to the latter is neglected. It is easily shown that the path difference between the direct and reflected rays at a point P′ is given by

$$\left.\begin{array}{l}\delta' = 2a\theta^3 - 2d\theta^2, \\ x' = 3a\theta^2/2 - 2d\theta\end{array}\right\} \qquad \text{(B)}$$

x' being equal to C′P′, and d=CC′. By putting $\delta' = n\lambda$ and eliminating θ, the positions of the minima of illumination may be calculated. A complete agreement of the results thus obtained with those found in experiment cannot, however, be expected, as the fringes are narrow and the modifications due to diffraction are

not negligible. As regards the fringes alongside the caustic due to the reflected rays, we cannot expect to find a complete agreement between their widths and those found from Airy's theory, so long as the latter is not fully applicable. The divergence, if any, should be most marked when the region of the caustic under observation is nearest the edge of the cylinder, and for the fringes which are farthest from the caustic,

20. The foregoing conclusions have been tested by a series of measurements made with the focal plane in various positions in advance of the edge. To prove that the boundary of the field within the shadow is the caustic and not the surface of the cylinder, measurements were made of the length $C'P_1$, the rays incident on the cylinder being a parallel pencil. The results are given below.

d in cm.	Observed value of $C'P_1$ in cm.	Calculated value of $C'P_1$ in cm.
0·8	0·00454	0·00433
0·13	0·00750	0·00733

The following shows the widths of the fringes in the neighbourhood of the caustic when the focal plane was 1 6 mm. in advance of the edge, and those calculated from Airy's theory.

Observed widths in cm. $\times 10^{-5}$	159,	69,	56,	51,	45,	43
Calculated from Airy's formula	155,	70,	57,	50,	46,	43

The agreement in both cases is satisfactory.

21. Table IV shows the results of measurements made of the fringes in the transition-stages when the focal plane was only a little in advance of the edge

and Airy's theory is inapplicabie. The observed results are in general agreement with the indications of theory set out in paragraph 19. It will be seen that the fringes farthest in the region of the shadow show a fair agreement with Airy's theory, and the others are more nearly in agreement with the widths calculated from formula (B.)

TABLE IV.

Widths of bright bands in cm. $\times 10^{-6}$

$a = 1{\cdot}54$ cm. $\lambda = 6562 \times 10^{-8}$ cm.

Observed widths.	Calculated [Airy's Formula].	Calculated [Formula (B)].	Observed widths.	Calculated [Airy's Formula].	Calculated [Formula (B)]
$d = {\cdot}2$ mm.			$d = {\cdot}4$ mm.		
1546	1550	—	1555	1550	—
852	696	894	777	696	754
722	570	777	628	570	674
672	504	705	590	504	636
622	461	637	566	461	594
590	429	602	500	429	543
$d = {\cdot}6$ mm.			$d = {\cdot}8$ mm.		
1513	1550	—	1466	1550	—
700	696	—	706	696	—
626	570	586	563	570	—
536	504	549	503	504	508
493	461	520	475	461	483
446	429	497	448	429	463

Summary and Conclusion.

22. C. F. Brush has published some observations of considerable interest on the diffraction of light by cylindrical edges. The views put forward by him to explain the phenomena, however, present serious difficulties and are open to objection. My attention was drawn to this subject by Prof. C. V. Raman at whose suggestion the present work was undertaken by me in order to find the true explanation of the effects and to develop a mathematical theory which would stand quantitative test in experiment. This has now been done, and in the course of the investigation various features of importance overlooked by Brush have come to light. The following are the principal conclusions arrived at: (*a*) The fringes seen in the plane at which the incident light grazes the cylinder are due to the simple interference of the direct and reflected rays, the position of the dark bands being given by the formula $x=\frac{3}{4}(2a)^{\frac{1}{3}}\cdot(n\lambda)^{\frac{2}{3}}$; (*b*) the fringes in a plane further removed from the source of light than the cylinder are of the Fresnel class due to the edge grazed by the incident rays, but modified by interference with the light reflected from the surface behind the edge. The positions of the dark bands in these fringes are given by the formulæ* $x=2d\theta+3a\theta^2/2$, $n\lambda=2d\theta^2+2a\theta^3$, from which θ is to be eliminated; (*c*) when the focal plane of the observing microscope is on the side of the cylinder towards the light, the direct and the reflected rays do not both cover exactly the same part of the field, and by putting the focal

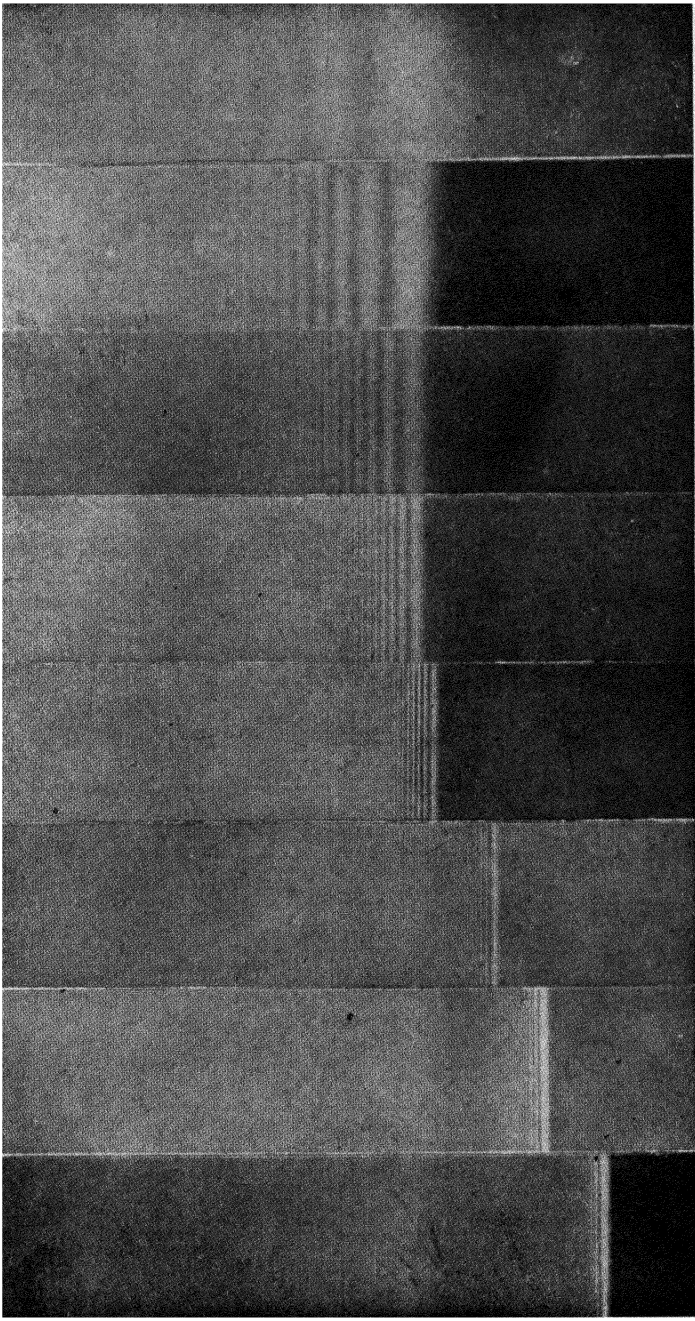
* This formula is subject to a small correction which is of importance only when d is large.

plane sufficiently forward towards the light, they may be entirely separated. When this is the case, the fringes of the ordinary Fresnel type due to the edge of the cylinder may be observed, and inside the shadow we have also an entirely separate system of fringes due to the reflected rays the first and principal maximum of which lie alongside the virtual caustic formed by oblique reflection ; the distribution of intensity in this system can be found from the well-known integral due to Airy; (*d*) but when the focal plane is only a little in advance of the edge, the caustic and the reflecting surface are nearly in contact, and Airy's investigation of the intensity in the neighbourhood of a caustic requires modification. It is then found that only a finite number of bands (one, two, three, or more according to the position of the plane of observation) is formed within the limits of the shadow, and not an indefinitely large number as contemplated by Airy's theory. The rest of the fringes seen in the field are due to the interference of the direct and reflected rays, but modified by diffraction at the edge of the cylinder.

The Indian Association
for the Cultivation of Science,
Calcutta, 1917.

Basu.

Plate



The Diffraction of Light by a Cylinder of radius 1·54 cm.

The Indian Photo Engraving Co., Calcutta.

PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

Vol. III. PART IV.

Friday, the 10th August, 1917 at 5 P.M. Rai Bahadur Dr. Chuni Lal Bose, I.S.O., Rasayanacharya, M.B., F.C.S.

Disappearance of volumes by dissolution of substances in water.

BY JITENDRA NATH RAKSHIT.

The fact that the curves for specific gravities and percentages of substances in water are neither straight nor simple, suggested that there must be some regular systematic cause which creates this complication. To discover the exact truth it became useful to consider the disappearance of volumes by the dissolution of substances in water. In several cases the number of disappeared volumes in 100 parts of *mixture* have been calculated but these data are, however, not strictly applicable for this purpose. Consequently the disappearances of volumes when a fixed quantity of substance is dissolved in increasing quantities of water are calculated by the following method.

Let 100 gms. of pure substance of specific gravity S be mixed with water of Wg gms. weight and specific

gravity Ws to produce (100+Wg) gms. of mixture of specific gravity S′. Then,

$$\text{Vol. of 100 gms. of pure substance} = \frac{100}{S} \text{ c.c.}$$

$$\text{,, ,, Wg ,, ,, water} = \frac{Wg}{Ws} \text{ c.c.}$$

$$\text{and ,, ,, (100+Wg) ,, mixture} = \frac{100+Wg}{S'} \text{ c.c.}$$

$$\text{Therefore, disappearance of volume} = \frac{100}{S} + \frac{Wg}{Ws} - \frac{100+Wg}{S'} \text{ c.c.}$$

$$= \text{K c.c. (say)}$$

When the gravities are measured at 4°C. compared with water at 4°C., $W_s = 1$. And when they are measured at t°C. compared with water at t°C., all the three above items are similarly influenced by the assumption of W_s at t°C. = 1; in this case this disappearance of volume will be at t°C. But when the gravities are taken at t°C. and compared with water at 4°C. then W_s = specific gravity of water at t°C. compared with water at 4°C., and the disappearance of volume found will be at t°C. Truly S in "$\frac{100}{S}$" is the specific gravity of the substance when it is in pure state before passing into solution, which is kept as such in cases of the gases or solids, "$\frac{100}{S}$" being a constant figure for particular substances.

For the construction of the following tables either specific gravity tables from "Landolt Bornstein—Physikalisch-chemische Tabellen" 3rd Edn. 1905, abbreviation for which is written as L, were used, or otherwise, as mentioned.

SULPHURIC ACID DOMKE. L. PAGE 326.

P. C. W/W.	Wg.	0/4		5/4		15/4		20/4	
		S′	K	S′	K	S′	K	S′	K
1	9900	1·0075	29·44	1·0073	26·64	1·0061	23·86	1·0051	22·90
5	1900	1·0364	24·44	1·0355	22·74	1·0332	20·42	1·0317	19·45
10	900	1·0735	22·56	1·0718	21·16	1·0681	19·04	1·0661	18·23
20	400	1·1510	19·64	1·1481	18·67	1·1424	17·15	1·1394	16·52
30	233·33	1·2326	16·93	1·2291	16·31	1·2220	15·23	1·2185	14·82
40	150	1·3179	14·33	1·3141	13·93	1·3065	13·41	1·3028	13·01
50	100	1·4110	12·26	1·4070	12·03	1·3990	11·61	1.3951	11·45
60	66·67	1·5154	10·69	1·5111	10·55	1·5024	10·27	1·4982	10·18
70	40·28	1·6293	8·19	1·6245	8·10	1·6151	7·94	1·6105	7·88
80	25	1·7482	7·50	1·7429	7·45	1·7324	7·34	1·7272	7·30
90	11·11	1·8361	5·11	1·8306	4·59	1·8198	4·54	1·8144	4·52
100	0	1·8517	0	1·8463	0	1·8357	0	1·8305	0

* NITRIC ACID. VELEY AND MANLEY. L. PAGE 325.

4/4			
P. C. W/W.	Wg.	S'	K
0·625	15900·00	1·0035	20·66
1·323	7458·57	1·0076	21·86
2·630	3702·28	1·0154	22·60
3·42	2821·67	1·0199	21·86
6·11	1535·18	1·0356	21·07
10·75	830·23	1·0644	21·14
21·95	355·58	1·1365	19·57
38·10	162·46	1·2500	17·34
51·24	95·16	1·3376	14·11
79·59	25·64	1·4750	5·31
95·62	4·58	1·5219	0·71
99·97	0	1·5420	0

* NITRIC ACID. LUNGE AND REY. L. PAGE 325.

15/4			
1·06	9333·96	1·0051	22·00
5·35	1769·16	1·0290	20·09
9·85	915·22	1·0554	19·88
18·16	450·66	1·1065	19·17
31·68	215·65	1·1953	17·54
60·37	65·64	1·3754	11·08
99·97	0	1·5204	0

* These two sp. gr. tables of nitric acid do not agree, apparently the first one seems to be wrong being itself irregular.

STANNIC CHLORIDE. GERLACH. L. PAGE 337.

15/15			
P. C. W/W.	Wg.	S′	K
10	900	1·082	20·55
20	400	1·174	18·87
30	233·33	1·279	17·48
40	150	1·404	16·70
50	100	1·556	16·23
70	40·28	1·973	13·95
100	0	2·234	0

FORMIC ACID. RICHARDSON. L. PAGE 355.

20/4			
1	9900·00	1·0020	19·36
4	2350·00	1·0094	7·87
10	900·00	1·0247	7·58
30	233·33	1·0730	4·97
50	100·00	1·1208	3·62
70	40·28	1·1656	1·88
80	25·00	1·1861	1·53
90	11·11	1·2045	0·77
100	0	1·2213	0

ACETIC ACID. OUDEMANS. L. PAGE 354.

P. C. W/W.	Wg.	*5/4		15/4		20/4	
		S'	K	S'	K	S'	K
1	9900·00	1·0017	11·74	1·0007	10.52	0·9997	9·78
5	1900·00	1·0083	11·23	1·0067	9·76	1·0055	9·56
10	900·00	1·0167	11·19	1·0142	9·58	1·0126	9·30
20	400·00	1·0325	10·50	1·0284	8·93	1·0261	8·69
30	233·33	1·0467	9·65	1·0412	8·15	1·0383	7·97
40	150·00	1·0590	8·69	1·0523	7·32	1·0488	7·15
50	100·00	1·0692	7·71	1·0615	6·44	1·0575	6·32
60	66·67	1·0771	6·69	1·0685	5·50	1·0642	5·43
70	40·28	1·0825	5·45	1·0733	4·39	1·0686	4·34
80	25·00	1·0847	4·52	1·0748	3·48	1·0699	3·47
90	11·11	1·0819	3·18	1·0713	2·17	1·0660	2·16
100	0	*Solid	0	1·0553	0	1·0497	0

* S in this case is assumed to be 1.0553 which is only true at 15/4.

METHYL ALCOHOL. DITTMAR AND FAWSITT. L. PAGE 357.

0/4			
P. C. W/W.	Wg.	S′	K
1	9900·00	0·9981	5·38
5	1900·00	0·9914	6·27
10	900·00	0·9843	7·56
20	400·00	0·9723	9·22
30	233·33	0·9606	9·75
40	150·00	0·9457	9·08
50	100 00	0·9287	8·08
60	66·67	0·9092	6·77
70	40·28	0·8869	5·53
80	25·00	0·8631	3·60
90	11·11	0·8375	1·87
95	5·62	0·8240	0·89
100	0	0·8102	0

ETHYL ALCOHOL. HEHNER. ANALYST. V.

15.5/15.5			
1	9900·00	0·9981	6·94
5	1900·00	0·9914	8·68
10	900·00	0·9841	9·82
20	400·00	0·9716	11·36
30	233·33	0·9578	11·29
40	150·00	0·9396	9·90
50	100·00	0·9182	8·16

ETHYL ALCOHOL. HEHNER. ANALYST. V. *ctd.*

15.5/15.5			
P. C. W/W.	Wg.	S'	K
60	66·67	0·8956	6·55
70	40·28	0·8721	5·40
80	25·00	0·8483	3·62
90	11·11	0·8228	2·04
95	5·26	0·8089	1·11
100	0	0·7938	0

PROPYL ALCOHOL. PAGLIANI. L. PAGE 360.

0/4			
10·0	900·00	0 9878	9·84
18·2	443·95	0·9805	11·22
25·0	300·00	0·9707	10·06
35·7	180·11	0·9511	7·72
40·0	150·00	0·9425	6·85
62·5	60·00	0·8974	3·71
86·9	15·07	0·8502	1·83
100	0	0·8190	0

ISO-BUTYL ALCOHOL. TRAUBE. L. PAGE 360.

20/4			
2	4900·00	0·9949	7·64
4	2400·00	0·9922	9·15
6	1566·67	0·9895	9·63
8	1150·00	0·9869	10·65
100	0	0·8029	0

ISO-AMYL ALCOHOL. TRAUBE. L. PAGE 360.

20/4			
P. C. W/W.	Wg.	S′	K
1	9900·00	0·9967	7·35
2	4900·00	0·9951	7·33
2·5	3900·00	0·9946	8·44
100	0	0 8121	0

GLYCERINE. NICOL. L. PAGE 366.

20/20			
5	1900·00	1·0118	2·47
10	900·00	8·0239	2·48
20	400·00	1·0488	2·41
25	300·00	1·0617	2·39
30	237·33	1·0747	2·31
40	150·00	1·1012	2·12
50	100·00	1·1283	1·89
60	66·67	1·1556	1·58
70	40·28	1·1829	0·83
80	25·00	1·2101	0·85
90	11·11	1·2372	0·44
100	0	1·2635	0

* GLYCERINE. LENZ.

12–14/12–14.			
P. C. W/W	Wg.	S'.	K.
1	9900·00	1·0025	3·73
2	4900·00	1·0049	3·18
5	1900·00	1·0123	3·10
10	900·00	1·0245	2·71
20	400·00	1·0498	2·51
30	233·33	1·0771	2·65
40	150·00	1·1045	2·45
50	100·00	1·1320	2·12
60	66·67	1.1582	1·57
70	40·28	1·1889	1·17
80	25·00	1·2159	0·99
90	11·11	1·2425	0·48
100	0	1·2691	0

ACETONITRILE. TRAUBE. L. PAGE 363.

15/4.			
2·73	3563·00	0·99570	14·13
5·25	1803·80	0·99289	14·60
8·22	1116·54	0·98865	13·78
12·51	699·36	0·98064	11·59
16·56	503·86	0·97427	11·25
100	0	0·7890	0

*Lewkowtisch Chemical Technology of Fats and Waxes, 3rd Edn., 1904, p. 1102.

ACETONE. SQUIBB. L. PAGE 366.

4/4.

P. C. W/W.	Wg.	S′.	K.
20	400·00	0·9794	13·34
30	233·33	0·9660	12·15
40	150·00	0·9527	11·44
50	100·00	0·9334	9·58
60	66·67	0·9106	7·49
70	40·28	0·8877	6·11
80	25·00	0·8626	3·94
90	111·11	0·8371	2·23
100	0	0·8082	0

15/15.

20	400·00	0·9755	12·98
30	233·33	0·9604	11·79
40	150·00	0·9554	11·09
50	100·00	0·9247	9·25
60	66·67	0·9019	7·41
70	40·28	0·8790	6·22
80	25·00	0·8536	4·10
90	11·11	0·8260	2·13
95	5·26	0·8113	1·05
100	0	0·7966	0

M. ELROY.

	15/4.		
P. C. W/W.	Wg.	S	K
10	900·00	0·9868	12·86
20	400·00	0·9744	12·65
30	233·33	0·9604	11·88
40	150·00	0·9449	10·98
100	0	0·7973	0

NICOTINE. PRIBRAM. L. PAGE 363.

	20/4.		
4·73	2014·16	1·0015	5·77
10·19	881·35	1·0054	5·90
20·75	381·93	1·0132	6·01
49·30	102·84	1·0329	5·67
62·81	59·21	1·0391	5·16
75·13	33·12	1·0394	4·15
86·89	15·09	1·0299	2·42
100	0	1·0095	0

AMMONIA. GRUNEBERG. L. PAGE 329.

	15/15.		
1·05	9423·81	0·995	$\frac{100}{S}$ – 147·85
2·15	4551·11	0·990	146·92
3·30	2930·30	0·985	146·14

AMMONIA. GRUNEBERG. L. PAGE 329.

15/15.

P. C. W/W.	Wg.	S′	K′
4·50	2122·22	9·980	$\frac{100}{S}$ – 145·33
5·75	1639·13	0·975	144·46
12·60	693·65	0·950	141·78
19·80	405·05	0·925	140·95
27·70	261·01	0·900	140·11
33·40	199·40	0·885	138·90

AMMONIA. WACHSMUTH. L. PAGE 329.

15/15.

1·17	8447·00	0·995	142·95
2·26	4324·78	0·990	144·61
3·48	2772·19	0·98	143·76
4·71	2023·14	0·980	143·32
5·97	1575·04	0·975	142·90
12·80	681·25	0·950	141·11
20·26	393·58	0·925	140·01
28·34	258·86	0.900	139·20
33·64	197·26	0.885	138·62

AMONIA. LUNGE. L. PAGE 329.

15/14.			
P. C. W/W.	Wg.	S'.	K
1·14	8671·93	0·995	$\frac{100}{S}$ – 136·34
2·31	4247·82	0·990	129·16
3·55	2716·90	0·985	140·46
4·80	1983·33	0·980	150·94
6·05	1552·06	0·975	140·99
20·18	395·54	0·925	139·86
30·03	233·00	0·895	138·87
35·6	180·90	0·880	138·14

AMMONIA. CARIUS. L. PAGE 329.

16/16.			
1·08	9159·28	0·995	146·52
2·35	4155·32	0·990	142·98
3·55	2716·90	0·985	142·89
4·75	2005·26	0·980	142·96
6·00	1566·66	0·975	142·74
12·65	690·51	0·950	141·59
20·00	400·00	0·925	140·54
29·00	244·82	0·900	138·31
35·65	180·55	0·885	136·45

HYDROCHLORIC ACID. LUNGE AND MARCHLEWSKI. L. PAGE 324.

15/4.			
P. C. W/W.	Wg.	S′	K
1·15	8595·65	1·0050	$\frac{100}{S}$ −48·99
1·52	6478·94	1·0069	49·07
2·93	3312·96	1·0140	49·92
5·18	1830·50	1·0251	51·11
12·38	707·75	1·0609	53·00
20·29	392·85	1·1014	54·27
31·28	219·69	1·1589	55·98
39·15	155·42	1·2002	57·25

CAUSTIC SODA. PICKERING. L. PAGE 329.

15/4.			
1	9900·00	1·0106	+13·65
2	4900·00	1·0219	+11·57
3	3233·33	1·0331	+ 9·49
4	2400·00	1·0443	+ 8·21
5	1900·00	1·0555	+ 6·83
10	900·00	1·1111	+ 0·72
20	400·00	1·2219	− 8·83
30	233·33	1·3312	−16·87
40	150·00	1·4343	20·30
50	100·00	1·5303	30·60

CAUSTIC POTASH. PICKERING. L. PAGE 329.

15/4.			
P. C. W/W.	Wg.	S'	K
1	9900·00	1·0083	$\frac{100}{S}$ −8·92
2	4900·00	1·0175	9·59
3	3233·33	1·0267	10·43
5	1900·00	1·0452	11·83
10	900·00	1·0918	15·10
20	400·00	1·1884	20·38
30	233·33	1·2905	24·76
40	150·00	1·3991	28·55
50	100·00	1·5143	31·98

3

SODIUM CHLORIDE. KARSTEN. L. PAGE 322.

P. C. W/W.	Wg.	0/4		15/4		20/4	
		$\dot{S}'$	$\dot{K}$	$\dot{S}'$	$\dot{K}$	$\dot{S}'$	$\dot{K}$
1	9900	1·0076	$\frac{100}{S} - 23{\cdot}58$	1·0064	$\frac{100}{S} - 27{\cdot}64$	1·0054	$\frac{100}{S} - 28{\cdot}77$
5	1900	1 0384	25·85	1·0355	29·75	1·0341	30·69
10	900	1·0771	28·32	1 0726	31·50	1·0707	32 38
20	400	1·1562	32·41	1·1497	34·52	1·1473	35·39
25	300	1·1972	34·09	...	...	1·1879	36·19

d. TARTARIC ACID. PRIBRAM. L. PAGE 356.

20/4.			
P. C. W/W.	Wg.	S.	K.
1·01	9800·99	1·0028	$\frac{100}{S}$ – 54·83
5·09	1864·64	1·0215	55·45
10·89	818·27	1·0491	55·57
20·70	383·09	1·0978	56·18
30·16	231·56	1·1486	56·71
44·33	125·58	1·2312	57·41
49·95	100·20	1·2655	57·81

CHLORAL HYDRATE. RUDOLPHI. L. PAGE 363.

20·2/4.			
0·5	19900·00	1·0012	–40·80
2·0	4900·00	1·0065	58·89
5·0	1900·00	1·0198	57·80
10·0	900·00	1·0440	56·26
20·0	400·00	1·0956	55·66
33⅓	200·00	1·1711	55·82
50	100·00	1·2713	57·13
66⅔	50·00	1·3998	57·06
80	25·00	1·5134	57·55

PHENOL. TRAUBE. L. PAGE 363.

15/4.			
1·14	8671·93	1·00037	89·72
2·20	4445·45	1·00133	89·66
5·18	1830·50	1·00418	90·34

CANE SUGAR. PLATO. L. PAGE 364.

0/4.			
P. C. W/W.	Wg.	S′	K
1	9900·00	1·0039	$\frac{100}{S}$ – 60·16
5	1900·00	1·02033	59·96
6	1566·67	1 02449	60·01
10	900·00	1·04135	60·20
20	400·00	1·08546	60·59
30	233·33	1·13274	60·93
40	150·00	1·18349	61·23
50	100·00	1·23775	61·57
60	66·67	1·29560	61·96
70	40·28	1·35719	63·04

* CANE SUGAR.

17·5/17·5.			
1	9900·00	1·00388	61·36
5	1900·00	1·0197	61·36
10	900·00	1·0401	61·44
20	400·00	1·0833	61·55
30	233·33	1·1297	61·73
40	150·00	1·1794	61·97
50	100·00	1·2328	62·23
60	66·67	1·2899	62·54
70	40·28	1·3509	62·94
80	25·00	1·4159	63·28
90	11·11	1·4849	63·71

* **Allen's Commercial Organic Analysis. Part I, 4th Edn. 1909, pages 292-295.**

* INVERT SUGAR. HERZFELD.

17·5/17·5.			
P. C. W/W.	Wg.	S′	K.
10	900·00	1·04034	$\frac{100}{S}$ - 61·22
15	566·67	1·06154	61·34
20	400·00	1·08357	61·43
25	300·00	1·10616	61·61

* LAVULOSE. LIPPMANN.

20/4.			
1·01	9800·99	1·0021	61·91
4·971	1911·48	1·0178	61·46
10·5199	850·48	1·0405	61·50
20·2638	393·49	1·0821	61·85
30·1157	232·83	1·1279	61·84

* ANHYDROUS DEXTROSE. SALOMON.

17·5/17·5.			
1·988	4930·18	1·0075	62·55
5·873	1602·77	1·023	61·72
10·570	846·07	1·042	61·85
15·984	525·62	1 0649	61·86

ANHYDROUS MALTOSE. SALOMON.

17·5/17·5.			
1·987	4932·71	1·00785	60·80
5·87	1603·57	1·02340	61·04
9·637	937·66	1·03900	61·05
18·587	432·63	1·07740	61·73
26·928	271·36	1·1155	61·55

* Allen's Commercial Organic Analysis. Part I, 4th Edn. 1909, pages 292-295.

CONCLUSIONS.

1. In some cases the increase of dilution cases the increase of disappearance of volumes ; but there are several others which are very remarkable, the disappearance of volumes increases at first with the dilution then after reaching maximum the disappeared volumes begin to reappear more and more as the dilution increases. Maximum gravities of solutions of some chemicals, and percentage contractions are offshoots of *this* cardinal principle.

2. The maximum contractions are constants and different for different substances. There are some similarities noticeable according to the similarity and gradation of chemical properties of them which are cleanly marked in the cases of alcohols.

3. It is evident in the cases of sulphuric acid, acetic acid and sodium chloride, that the disappearance of volumes at all dilutions diminishes as the temperature rises. It is, however, not yet ascertained whether this apparent re-appearance of volume is due to the differences of co-efficients of expansion of water and the substance or to the decrease of the intensity of cause effecting the contraction. It remains as a subject for further investigation.

OPIUM FACTORY,
Ghazipur, U. P.

On the Application of Cochineal Stain on Calcite and Aragonite.

By Sureschandra Datta, M.Sc.,

Professor of Chemistry Ripon College, Calcutta.

In a previous communication ([1]) I have described the application of aniline black as a stain to distinguish between calcite and aragonite and it has been found that with the help of aniline black these two natural carbonates can be very easily distinguished. So far as I am aware cochineal too has never been used to differentiate between calcite and aragonite and this note is meant to put on record the results I have obtained by staining calcite and aragonite with cochineal in presence of some acids and salts.

The way in which the stain has been fixed on calcite and aragonite is very simple. These minerals are separately powdered. Each is boiled in sufficiently dilute solutions of some salts and acids as mentioned below and in the latter case care must be taken so that the carbonate powders are not completely lost in the acids. Cochineal solution of sufficient strength is added next and the whole thing is boiled again when the powders of the minerals under examination are observed to have stains fixed on them. There is always some difference between the stains assumed by calcite and aragonite. The stains fixed are observed under the boiling solutions which are poured off and the stained minerals are washed with hot water and the stains whether fixed or not and their intensities whether decreased or not are taken notice of. It is not out of place to add here that when the minerals under examination are heated separately with sufficiently strong cochineal solution only, there are observed no stains on the said minerals.

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(1) *On the staining of Calcite and Aragonite by means of Aniline black*—read in the Third Quarterly Meeting of the Indian Association for the Cultivation of Science, 23rd September, 1916.

The following is the table of the results of my experiments—the experiments being conducted on the method outlined above :—

The acid or salt in which calcite and aragonite are separately boiled before the addition of strong cochineal solution in which the minerals are boiled again.	Stains under the hot solutions on calcite and aragonite.	Stains after washing with hot water on calcite and aragonite.	Colour of precipitate, if any.	Difference between the stains on calcite and aragonite.
Ammonium-Fluoride	Cal.–Deep blue-black. Ara.–Light blue-black.	Same. Intensities slightly decrease.	Cal.–Deep blue-black Ara.–Light blue-black.	A.
Ammonium-Molybdate	Cal.–Deep rose or lilac. Ara. Pink.	Same. Intensities slightly decrease	No precipitate.	A.
Ammonium-acetate	Cal.–Blue-black Ara.–Bluish with reddish.	Same. Intensities slightly decrease.	Cal.–Blue-black. Ara.–dirty red.	A.
Ammonium-bromide	Cal.–Deep rose Ara.–Light rose or pink.	Same. Intensities slightly decrease.	No precipitate.	C. But there is difference enough to differentiate the two minerals by means of stains.

The acid or salt in which calcite and aragonite are separately boiled before the addition of strong cochineal solution in which the minerals are boiled again.	Stains under the hot solutions on calcite nnd aragonite.	Stains after washing with hot water on calcite and aragonite.	Colour of precipitate, if any.	Difference between the stains on calcite and aragonite.
Barium chloride	Cal.–Blue. Ara.–Bluish with reddish.	Same.	No precipitate.	B.
Sulphuric acid	Cal.–Bluish. Ara.–Reddish.	Same. Intensities decrease. On heating with cochineal solution again:— Cal.–Deep red. Ara.–Light red.	Cal.–Blue black. Ara.–Dirty reddish.	A.
Hydrochloric acid	Cal.–Bluish. Ara.–Violet.	Same. The colour on aragonite becomes intense on washing with hot water.	Cal.–Blackish green. Ara.–Brownish green.	A.

The acid or salt in which calcite and aragonite are separately boiled before the addition of strong cochineal solution in which the minerals are boiled again.	Stains under the hot solutions on calcite and aragonite.	Stains after washing with hot water on calcite and aragonite.	Colour of precipitate, if any.	Difference between the stains on calcite and aragoinite.
Nitric acid	Cal.–Bluish. Ara.–Reddish.	Same. On treating with cochineal solution :— Cal.–Slightly red. Ara.–Very light red	Cal.–Grayish. Ara.–Dirty Red.	A.
Acetic acid	Cal.–Blue. Ara.–Reddish.	Same.	Cal.–Blue-black Ara.–Dirty red	A.
Formic acid	Cal.–Blue. Ara.–Bluish with reddish.	Intensities decrease to a great extent. On treating with cochineal :— Cal.–Red. Ara.–Bluish.	Cal.–Grayish blue-black. Ara.–Dirty red	A.

The acid or salt in which calcite and aragonite are separately boiled before the addition of strong cochineal solution in which the minerals are boiled again.	Stains under the hot solutions on calcite and aragonite.	Stains after washing with hot water on calcite and aragonite.	Colour of precipitate, if any.	Difference between the stains on calcite and aragonite.
Lactic acid	Cal.–Blue. Ara.–Bluish with reddish.	Same. On treating with cochineal :— Cal.–Red Ara.–Reddish	Cal.–Grayish blue black. Ara.–Dirty reddish.	A.
Oxalicacid	Cal.–Blue. Ara.–Reddish.	Same.	No precipitate.	C.
Silver nitrate By silver nitrate solution calcite and aragonite are distinguished as mentioned in current literature (1) But cochineal solution with silver nitrate has never been used before.	Cal.–Black. Ara.–Brownish black.	Same. Intensities decrease	No precipitate.	A.
Ammonium phosphate	Cal.–Bluish Ara.–Very light bluish.	Same.	No precipitate.	C.

(1) Doelter—*Petrogenesis*, Bd. 1, p 112.

N. B. A—Very pronounced. B—Pronounced. C—Not very pronounced. The stains on the powders of calcite and aragonite are better distinguished under water than when they are dry.

A new Process for the Carbonisation of sea weeds.

(Abstract.)

BY DR. RASIK LAL DATTA, D.Sc.

This process relates to the carbonisation of weeds in a closed chamber in a regulated current of air and passing the products of combustion through a spiral condenser for the condensation of tar which is formed in good quantity by the heat of the carbonisation and finally leading the gas through a scrubber in which a solution of alkali is allowed to trikle down. The iodine which is volatilised during the carbonisation is kept back in the condenser and the last traces in the scrubber. The iodine from tar and the alkaline solution may be recovered in any known manner.

PROCEEDINGS

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FOR THE

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1917.

PROCEEDINGS

OF THE

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE.

Vol. III. PART V.

On the Flow of Energy in the Electromagnetic Field surrounding a Perfectly Reflecting Cylinder.

BY T. K. CHINMAYANANDAM, B.A. (HONS.),
Research Scholar in the Indian Association for the Cultivation of Science, Calcutta.

§ 1. *Introduction.*

In a paper recently contributed to this journal,* Mr. N. Basu has discussed the general features of the phenomena observed in the immediate neighbourhood of a perfectly reflecting cylinder, on which plane light waves are incident in a direction at right angles to its axis. Further investigation was, however, necessary in order to establish the formulæ for the distribution of light intensity in the various parts of the field. These formulæ have now been obtained, and subjected to a detailed experimental test. Besides describing the results of a photometric study that has been carried out, the present paper also deals with the form of the

* N. Basu.—*On the Diffraction of Light by Cylinders of large Radius*, Proc. of the Ind. Association, Vol. III, part 3, 1917.

lines of flow of energy through the field, which, it is thought, may prove of interest with reference to the work of Profs. R. W. Wood* and Max Mason† on the simpler case of the interference field due to two point sources of light.

It may be remarked here that the phenomena, which form the subject of this paper may be strikingly shown on a large scale, without the aid of a microscope, by using a cylindrical surface of very large radius as the diffracting "edge." A strip of thick plate glass, two inches wide and about a yard long, may be bent into a circle of some yards radius by resting it on supports near the two ends, and loading the latter sufficiently. A slit illuminated by a Cooper-Hewitt lamp and placed at some distance from the surface in a line with it, may be used as the source of light. A very large number of fringes may then be seen with a low-power eye-piece, if the plane of observation be within a few feet of the cylindrical "edge." At greater distances, the fringes widen out; their visibility and number decrease, and their spacing alters with increasing distances from the cylinder in such manner as to approximate more and more closely to that of the diffraction fringes due to a straight edge. Some photographs which have been taken with the arrangement described above are shown in Plate VI, where figures (a), (b), and (c) correspond to the phenomena in planes at increasing distances from the edge.

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* R. W. Wood.—*On the Flow of Energy in a System of Interference Fringes*, Phil. Mag., 18, p. 250.

† Max Mason.—*The Flow of Energy in an Interference Field*, Phil. Mag., 20, p. 290.

§ 2. *The Form of the Illumination Curves.*

Debye* has shown from the electro-magnetic theory, that at a great distance from a cylinder (assumed to be of large radius) on which plane waves are incident, the disturbance due to it is practically the same as that to be expected from the principles of geometrical optics, this statement however not being taken as correct in respect of points lying in a direction very nearly the same as that of the incident rays. Debye's results suggest a simple method of finding the distribution of intensity at points lying within the region of light, in the immediate neighbourhood of the cylinder. Let AOB (Fig. 1) represent the section of the

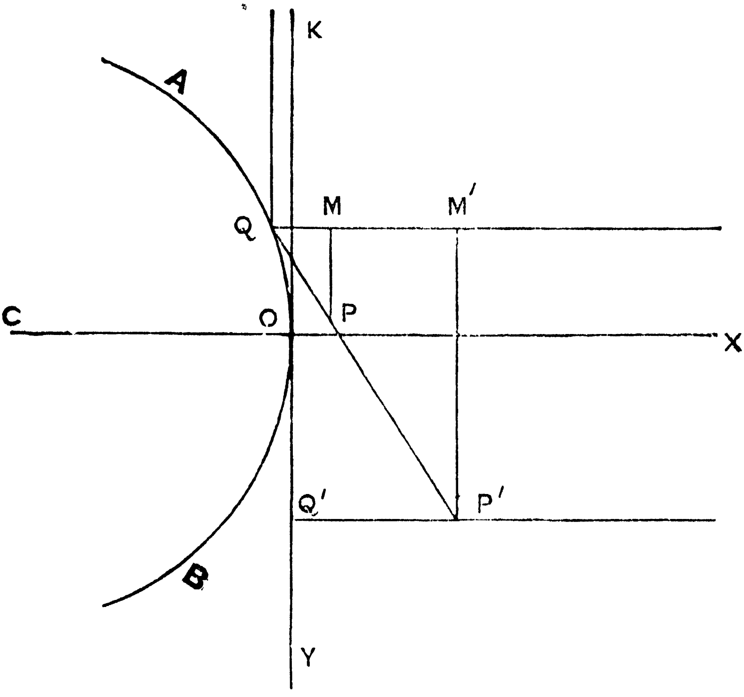


Fig. 1

* Debye.—Phys. Zeitschr., 9, pp. 775-778, Nov., 1908; also Science Abstracts, 1909, p. 88.

cylinder, and KOY the direction of the incident rays. We may assume that the fringes observed in the plane OX containing the edge of the cylinder grazed by the rays, are due solely to the interference of these rays with those reflected from the surface of the cylinder at varying angles. This would also be the case as regards any plane such as QR in advance of the edge. But the phenomena in a plane such as Q′P′ which lies on the remote side of the edge, would not admit of such simple treatment, especially when we consider the effect at points lying not far from the boundary OY of the direct and reflected rays. In such a plane, the intensity at any point on the right of the boundary may be regarded as due to the superposition of three factors, *(a)* the effect due to the direct rays, *(b)* that due to the reflected rays, and *(c)* a diffraction effect mainly perceptible in the neighbourhood of the boundary. If the cylinder were replaced by a perfectly reflecting semi-infinite screen lying in the plane CO with its edge at O, the diffraction effect would be found as in Sommerfeld's well-known investigation,* by superposing upon the direct rays, a radiation emitted by the edge of the screen. It will be observed that in the present case, the intensity of the rays regularly reflected from the cylinder, as given by the formulæ of Geometrical Optics, is zero along the boundary OY, increasing slowly as we move away from the boundary into the region of light, and thus presents no discontinuity. It thus seems justifiable to assume that so far as regards the phenomena in the region on the

* Sommerfeld.—*On the Math. Theory of Diffraction,* Math. Annalen, Vol. XLVII, p. 317, 1895.

right-hand side of the boundary, the diffraction effect (*c*) is practically the same as in the case of a semi-infinite screen with its edge at O.

The distribution of intensity in the field may be readily found on the foregoing assumptions. Take the edge O as origin of co-ordinates, and rectangular axes OX, OY, perpendicular and parallel respectively to the direction of the incident rays, and let the angle OCQ, assumed to be small, be denoted by θ. The path difference between the direct and the reflected rays reaching any point P is

$$\delta = 2\pi/\lambda\ (QP-MP)+\pi$$

$$= 2k\theta^2\ (y+a\theta)+\pi \quad \text{approximately,}$$

if k be written for $2\pi/\lambda$.

Again, if the amplitude of the incident light be taken as unity, that of the reflected light may be written as

$$\left(\frac{\rho}{\rho+QP}\right)^{\frac{1}{2}}$$

where ρ is the radius of curvature of the reflected wave on emergence at Q. Since

$$\rho = \frac{a\theta}{2} \quad \text{approximately}$$

$$\frac{\rho}{\rho+QP} = \frac{a\theta}{2y+3a\theta}$$

In any plane in advance of that passing through the edge of the cylinder ($y = -d$, say), the expression for the intensity of illumination at any point is

$$I = 1+s-2\sqrt{s}\cos\phi \quad \ldots \quad \ldots \quad (1)$$

where $\phi = 2k\theta^2\ (y+a\theta)$

and $s = \dfrac{a\theta}{3a\theta+2y}$.

The positions of the maxima and minima of illumination are given by

$$\frac{dI}{d\theta}=\frac{ds}{d\theta}\left(1-\frac{\cos\phi}{\sqrt{s}}\right)+2\sqrt{s}\sin\phi\,\frac{d\phi}{d\theta}=0. \qquad \ldots \qquad (2)$$

Since $\frac{d\phi}{d\theta}=4k\theta(y+a\theta)+2ka\theta^2$, and contains the factor $2\pi/\lambda$, it will be large, so that the first term in equation (2) is negligible. That equation can hence be written

$$\sin\phi=0.$$

$$\text{or} \qquad 2\theta^2(y+a\theta)=m\lambda/2 \quad \ldots \qquad \ldots \quad (3)$$

while the relation between θ and x is given by

$$x=(y+a\theta)2\theta-a\theta^2/2$$

$$=2y\theta+3a\theta^3/2. \quad \ldots \qquad \ldots \qquad \ldots \quad (4)$$

From (1) and (3) it, is seen that the intensities of the successive maxima and minima are respectively proportional to

$$I_{\text{max.}}=\left\{1+\left(\frac{a\theta}{3a\theta-2d}\right)^{\frac{1}{2}}\right\}^2$$

$$I_{\text{min.}}=\left\{1-\left(\frac{a\theta}{3a\theta-2d}\right)^{\frac{1}{2}}\right\}^2$$

The intensity curve has been plotted out in Plate I (*a*) for the case $a=1\cdot5$ cm. and $d=0\cdot2$ cm. It will be seen that in this plane $I_{\text{max.}}$ begins nearly with a value $(1+1)^2=4$, and drops down gradually in successive fringes to a limiting value of $\left(1+\frac{1}{\sqrt{3}}\right)^2=2\cdot49$. $I_{\text{min.}}$ incr eases from a value nearly zero to a limiting value $\left(1-\frac{1}{\sqrt{3}}\right)^2=0\cdot18$. The 'visibility' of the successive fringes in the plane of observation, therefore, decreases slowly.

At the plane $y=0$, the illumination is given by

$$I=1+\tfrac{1}{3}-\frac{2}{\sqrt{3}}\cos\phi \qquad \ldots \qquad \ldots \quad (5)$$

The intensity curve is shown in Plate I (*b*). $I_{\text{max.}}$

has a constant value of $\left(1+\frac{1}{\sqrt{3}}\right)^2$, and $I_{min.}$ a value $\left(1-\frac{1}{\sqrt{3}}\right)^2$. The 'visibility' of the fringes is thus stationary along this plane for a considerable distance from the edge.

Passing on to consider the distribution of Intensity in any plane Q′P′ below the plane $y=0$, we have, as remarked above, to add to the effect of the direct and the reflected rays a diffraction effect. We shall represent the latter effect by that due to a single source placed at the edge O, the amplitude of the disturbance due to it, at a point in the region bounded by OX and OY being given by Sommerfeld's expression*

$$\frac{1}{4\pi}\sqrt{\frac{\lambda}{r}}\cos\left(kr-nt+\frac{\pi}{4}\right)\left\{\pm\frac{1}{\cos\frac{\varphi+\varphi'}{2}}-\frac{1}{\cos\frac{\varphi-\varphi'}{2}}\right\} \quad (6)$$

where r is the distance of the point from the edge O, φ, φ' are the angles which the diffracted and the incident beams respectively make with the direction XO.

If we denote the angle P′OY by α

$$\varphi=3\pi/2-\alpha \quad \varphi'=\pi/2.$$

so that expression (6) becomes

$$\frac{1}{4\pi}\sqrt{\frac{\lambda}{r}}\cos\left(kr-nt+\frac{\pi}{4}\right)\left(\pm 1-\frac{1}{\sin\frac{\alpha}{2}}\right)$$

$$=-\frac{1}{4\pi}\,\frac{2}{\alpha}\sqrt{\frac{\lambda}{r}}\cos\left(kr-nt+\frac{\pi}{4}\right),$$

since α is small so far as our investigation is concerned.

Now $r=\text{P}'\text{O}=y+\frac{x^2}{2y}$; $\alpha=\frac{x}{y}$, approximately,

* Sommerfeld—*loc. cit.*

so that the above expression reduces to

$$-\frac{\sqrt{y\lambda}}{2\pi x}\cos\left(k.\overline{y+\frac{x^2}{2y}}-nt+\frac{\pi}{4}\right)\quad\text{(approx.).}$$

The total disturbance at P′ is thus

$$\xi=\cos(ky-nt)-\sqrt{s}\cos(ky-nt+k\,\overline{2a\theta^3+2y\theta^2})$$
$$-\frac{\sqrt{y\lambda}}{2\pi x}\cos\left(k.\overline{y+\frac{x^2}{2y}}-nt+\frac{\pi}{4}\right).$$

Remembering that, since $x=3a\theta^2/2+2y\theta$, $\frac{x^2}{2y}=2y\theta^2+3a\theta^3$ we get for the intensity of illumination at any point, the expression $I=1+S-2\sqrt{S}\cos\chi$ ... ... (7)

where $S=s+\frac{y\lambda}{4\pi^2x^2}+\frac{\sqrt{sy\lambda}}{\pi x}\cos\left(ka\theta^3+\frac{\pi}{4}\right)$ ... (8)

$$\chi=k\,(2a\theta^3+2y\theta^2)+\epsilon\quad\ldots\quad\ldots\quad\ldots\quad(9)$$

and $\tan\epsilon=\dfrac{\frac{\sqrt{y\lambda}}{\pi x}\sin\left(ka\theta^3+\frac{\pi}{4}\right)}{2\sqrt{s}+\frac{\sqrt{y\lambda}}{\pi x}\cos\left(ka\theta^3+\frac{\pi}{4}\right)}$ ... ... (10)

Equations (4) and (7) give for the positions of the maxima and minima of illumination

$$\left.\begin{aligned}3a\theta^2/2+2y\theta&=x\\2a\theta^3+2y\theta^2&=m\lambda/2-\frac{\epsilon\lambda}{2\pi}\end{aligned}\right\}\quad\ldots\quad\ldots\quad(11)$$

We see that the introduction of the diffraction term has slightly changed the positions of the maxima and minima. The magnitude of the change depends upon ϵ. which is zero when $y=0$ (equation 10), and steadily increases with y to a limiting value of $\left(ka\theta^3+\frac{\pi}{4}\right)$ or $\frac{\pi}{4}$ since $ka\theta^3$ is negligible over the first few bands when y is sufficiently large. By actual calculation it is found that this limit is practically reached, when y is over three times the radius of the cylinder. Under these conditions, equations (11) reduce to

$$x^2=y\lambda(4m-1)/4.\quad\ldots\quad\ldots\quad(12)$$

Formula (12) is identical with Schuster's formula for the case of diffraction of plane waves by a straight edge.

Returning to equation (7), we see that the intensity of illumination of the successive maxima and minima is given by

$$\left.\begin{aligned} I_{max.} &= (1+\sqrt{S})^2 \\ I_{min.} &= (1-\sqrt{S})^2 \end{aligned}\right\} \quad \ldots \quad \ldots \quad (13)$$

where S is given by equation (8).

The intensity curve for a plane 5 mm. behind the "edge" is shown in Plate I (*c*). It will be seen that the ratio of the minima to the maxima is considerably greater than in (*a*) and (*b*). Calculation also shows that the visibility of the successive fringes in this plane of observation should decrease, though somewhat slowly. For still greater distances from the edge of the cylinder, the illumination curves become practically identical with that of the Fresnel type due to a straight edge, the intensity of the reflected rays becoming negligible in comparison with that of the incident and the diffracted rays The ordinates of the curves (*a*), (*b*), and (*c*), (though not the abscissæ) have all been drawn to the same scale, and the curves illustrate the fact that the luminosity of the field as a whole decreases as we recede from the cylinder.

§ 3. *Photometric Study of the field.*

The formulæ obtained above have been tested by two independent methods—(1) by photometric comparison of the maxima and minima of illumination, and (2) by determination of their relative positions.

A small polished cylinder of glass, of about 1·5 cm. radius, was used. It was mounted on one of the

stands of an optical bench, and a microscope objective mounted on another of those stands was brought up close to the cylinder. Light from a narrow slit was passed through a collimating lens and was allowed to fall grazingly on the cylinder. The field was viewed through a micrometer eye-piece, placed at a distance behind the objective. By moving the cylinder towards or away from the objective, the phenomena at different planes $y=d$ could be observed.

The photometric arrangement used to study the relative intensity of the fringes was based on a Polarization method. The beam of light was plane polarized by passage through a Nicol before falling on the cylinder. The eye-piece, (a low-power one) was moved off to a pretty large distance behind the objective, and two narrow slits cut out of aluminium foil and pasted on two glass strips, were mounted, one above the other, between the eye-piece and the objective, so as to allow a small relative motion which could be controlled by a micrometer-screw. A thin mica plate was also fixed up on the upper one (which was movable in the actual experiment), the thickness of the plate and its orientation with respect to the slit being adjusted by trial so that, under the conditions of the experiment, it circularly polarized the light falling on it. The field was viewed through another Nicol fitted with a graduated circle and mounted just behind the slits.

The lower slit was always set on the first bright band, while the upper one was set successively on the different maxima and minima. Equality of illumination of the upper and lower slits was obtained in each case, by rotating the analysing Nicol. The reading for the

crossed position of the analyser being also taken, the ratio of the intensities of illumination could be easily calculated Thus if ψ be the orientation of the analyser in any case (ψ being reckoned from the crossed position) and I, I_0 the intensities of illumination of the upper and lower slits respectively,

$$I/I_0 = \sin^2\psi.$$

Readings were taken for the first few bands on the planes (1) y=0, (2) y=0·5 cm., and are shown in Table I with the corresponding values calculated from theory.

TABLE I.

n	y=0.				y=0·5 *cm.*			
	MAXIMUM.		MINIMUM.		MAXIMUM.		MINIMUM.	
	I_n/I_0.		I_n/I_0.		I_n/I_0.		I_n/I_0.	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
1	1·00	1·00	0·09	0·07	1·00	1·00	0·46	0·42
2	0·96	1·00	0·08	0·07	0·91	0·93	0·45	0·44
3	1·00	1·00	0·12	0·07	0·91	0·91	0·52	0·46
4	0·94	1·00	0·15	0·07	0·83	0·90	0·52	0·46

The discrepancies are within the limits of experimental error, so that the theory developed above appears to be substantially correct.

As has been remarked already, the theory was also tested by measurements of the positions of the minima of illumination in different parts of the field. Some explanation is here necessary with regard to the measurements of fringes in a plane in advance of the "edge" (y negative). With the ordinary arrangement

as described above, if the microscope is moved near, so that its focal plane may be in advance of the edge, we are unable to see the exact phenomena in that plane, since the light has to come past the "edge" before it can fall on the objective; and secondly, as has been fully described in Mr. Basu's* paper, the field is complicated by the occurrence of the caustic and its accompanying fringes, formed by reflection from the surface of the cylinder. This difficulty was got over in the present work by turning the cylinder around its axis, till the desired plane of observation coincided with the boundary of the polished surface. What is meant may be better understood by a reference to fig. 1, the process described being equivalent to cutting off the cylinder along CQ and removing the lower half. It is not easy, however, with this arrangement, directly to determine the value of y when it is negative; and in Table II below it has been obtained by calculation from a pair of readings. The source of light was a quartz mercury lamp with a green ray filter.

TABLE II.

Fringes between the Cylidrical Edge and the Source of light.

	$y=0$		$y=-2{\cdot}0$ mm.		$y=-2{\cdot}9$ mm.	
n	$x_n - x_1$.		$x_n - x_1$.		$x_n - x_1$.	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
3	0·0169	0·0169	0·0082	0·0082	0·0062	0·0060
5	0·0307	0·0302	0·0165	0·0163	0·0123	0·0120
7	0·0420	0·0417	0·0240	0·0240	0·0183	0·0182
9	0·0524	0·0522	0·0310	0·0317	0·0235	0·0235
11	0·0620	0·0619	0·0378	0·0395	0·0290	0·0293
			mms.			

* Basu—*loc. cit.*

TABLE III.

Fringes behind the Cylindrical Edge.

n	d=0·1 cm.		d=0·3 cm.		d=0·5 cm.		d=0·7 cm.	
	$x_n - x_1$.		$x_n - x_1$.		$x_n - x_1$.		$x_n - x_1$.	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
2	0·0159	0·0158	0·0250	0·0251	0·0341	0·0326	0·0370	0·0370
3	0·0284	0·0284	0·0439	0·0450	0·0580	0·0580	0·0660	0·0661
4	0·0385	0·0390	0·0600	0·0609	0·0776	0·0782	0·0887	0·0897
5	0·0483	0·0480	0·0740	0·0750	0·0928	0·0938		
6	0·0568	0·0570	0·0867	0·0879	0·1116	0·1134		
7	0·0651	0·0650	0·0990	0·0997				
8	0·0715	0·0723	0·1108	0·1110				
9	0·0794	0·0796						
10	0·0862	0·0863						

λ=5461. A. U.; a=1·54 cm.

The agreement between the calculated and the observed values is very close and confirms the theory.

§ 4. *The Loci of maxima and minima of Illumination.*

These curves have an interesting property which may be briefly considered here. The equation to the loci is obviously

$$r\,(1-\cos 2\theta) = n\lambda/2$$

or $$r\theta^2 = n\lambda/4 \quad \text{approx.} \quad \ldots \quad (14)$$

where r is the distance of the point from the surface of the cylinder measured along the reflected ray which passes through the point. The shape of the curves is indicated in Plate II (thick lines), for the case when $a=5$ inches, $\lambda=\cdot016$ inch, λ being taken so large for convenience of representation to scale; only the 1st, 3rd, 5th &c., loci are shown.

The equation to the loci can also be got in terms of θ, and x or y. Thus on eliminating y from equations (3) and (4) we get

$$x = \frac{m\lambda}{2\theta} - \frac{a\theta^2}{2} \quad \ldots \quad \ldots \quad (15)$$

which gives the abscissæ of the points at which the loci cut the straight lines $\theta=$ const.

The ordinates of these points are given by

$$2y\theta = x - \frac{3}{2}a\theta^2 = \frac{m\lambda}{2\theta} - 2a\theta^2$$

$$\therefore \quad y = \frac{m\lambda}{4\theta^2} - a\theta. \quad \ldots \quad \ldots \quad \ldots \quad (16)$$

From (15) and (16) it is seen that

$$dx = -\left(\frac{m\lambda}{2\theta^2} + a\theta\right)\delta\theta,$$

and $$dy = -\left(a + \frac{m\lambda}{2\theta^3}\right)\delta\theta$$

so that $$\frac{dy}{dx} = \theta$$

At any point, therefore, the curves bisect the angle between the directions of the direct and the reflected rays which pass through that point.

As might be expected, the formulæ obtained above for the case of diffraction by a cylinder, reduce to the ordinary formulæ for diffraction by a straight edge, on writing $a=0$, provided, of course, that the light from the other side of the cylinder is cut off by a semi-infinite plane extending to the left of the origin O.

For then, equations (11) become

$$\left.\begin{aligned} x &= 2y\theta \\ m\lambda/2-\epsilon\lambda/2\pi &= 2y\theta^2 \end{aligned}\right\}$$

and $\epsilon=\frac{\pi}{4}$, so that $x^2=y\lambda\,(4m-1)/4$.

which is Schuster's formula for diffraction of plane waves at straight edge. The results regarding the loci of maxima and minima will also apply for diffraction at a straight edge, under the same conditions.

§ 5. *On the flow of energy in the field.*

We will first take into account only the effects due to the interference of the direct and the reflected rays. The effect due to diffraction at the edge of the cylinder can be brought in later as a correction.

Let us assume, for simplicity, that the light is polarized in the plane of incidence, so that the electric intensity is perpendicular to that plane, and the magnetic intensity lies in it. Then at any point P (fig. 1.) the resultant electric intensity is

$$E=\left[\cos n\left(t-\frac{r_1}{c}\right)+\left(\frac{\rho}{\rho+r_2}\right)^{\frac{1}{2}}\cos\left\{n\left(t-\frac{r_2}{c}\right)+\pi\right\}\right]$$

where $r_1=PM$, $r_2=PQ$ and ρ is the radius of curvature

of the reflected wave at Q. The expression $\left(\frac{\rho}{\rho+r_2}\right)^{\frac{1}{2}}$ will in the rest of the paper be denoted by K. The resultant magnetic intensity at P is

$$\mathbf{H}=\overrightarrow{\cos n\left(t-\frac{r_1}{c}\right)}+\overrightarrow{\mathrm{K}\cos\left\{n\left(t-\frac{r_2}{c}\right)+\pi\right\}}$$

Let now $\mathbf{k}_1$, $\mathbf{k}_2$ be unit vectors at P in the direction of the direct and the reflected rays respectively. The flow of energy is determined by the Poynting vector S where

$$\mathrm{S}=\frac{c}{4\pi}\Big[\mathrm{EH}\Big]=\frac{c}{4\pi}\left\{\cos n\left(t-\frac{r_1}{c}\right)+\mathrm{K}\cos\left\{n\left(t-\frac{r_2}{c}\right)+\pi\right\}\right\}$$

$$\times\left\{\mathbf{k}_1\left[\cos n\left(t-\frac{r_1}{c}\right)\right]+\mathbf{k}_2\left[\mathrm{K}\cos n\left(t-\frac{r_2}{c}\right)+\pi\right]\right\},$$

$$\text{or}\ \frac{4\pi\mathrm{S}}{c}=\mathbf{k}_1\left[\cos^2\chi+\mathrm{K}\cos\chi\cos\chi'\right]+\mathbf{k}_2\left[\mathrm{K}\cos\chi\cos\chi'+\mathrm{K}^2\cos^2\chi'\right]$$

where $\chi=n\left(t-\frac{r_1}{c}\right)$ and $\chi'=n\left(t-\frac{r_2}{c}\right)+\pi$.

The time-mean $\overline{\mathrm{S}}$ of the flow of energy is given by

$$\frac{4\pi\overline{\mathrm{S}}}{c}=\tfrac{1}{2}\,\mathbf{k}_1\left[1+\mathrm{K}\cos(\chi'-\chi)\right]+\tfrac{1}{2}\,\mathbf{k}_2\left[\mathrm{K}^2+\mathrm{K}\cos(\chi'-\chi)\right]$$

$$\frac{8\pi\overline{\mathrm{S}}}{c}=\mathbf{k}_1\Big[a_1\Big]+\mathbf{k}_2\Big[a_2\Big]$$

if $a_1=1+\mathrm{K}\cos(\chi-\chi')$ and $a_2=\mathrm{K}^2+\mathrm{K}\cos(\chi'-\chi)$

If φ be the angle which the direction of $\overline{\mathrm{S}}$ makes with that of the incident rays, it can be easily shown that

$$\tan\varphi=\frac{a_2\sin 2\theta}{a_1+a_2\cos 2\theta}=\frac{2a_2\theta}{a_1+a_2}$$

since θ is small.

$$\text{Thus}\quad \tan\varphi=\frac{2\theta\left\{\mathrm{K}^2+\mathrm{K}\cos(x'-\chi)\right\}}{1+2\mathrm{K}\cos(\chi'-\chi)+\mathrm{K}^2}\quad\cdots\quad\cdots\quad(17)$$

now $\chi' - \chi = \frac{n\,(r_2 - r_1)}{c} + \pi \quad = \frac{n}{c} 2r_2\theta^2 + \pi.$

Hence equation (17) becomes

$$\tan\varphi = \frac{2\theta\left\{ K^2 - K\cos\frac{n}{c}2r_2\theta^2 \right\}}{1 + K^2 - 2K\cos\frac{n}{c}2r_2\theta^2} \quad \ldots \quad \ldots \quad (18)$$

The current of energy at the point is

$$\bar{S} = \frac{c}{8\pi}\left\{ a_1^2 + a_2^2 + 2a_1a_2\cos 2\theta \right\}^{\frac{1}{2}}$$

$$= \frac{c}{8\pi}\left(1 + K^2 - 2K\cos\frac{n}{c}2r_2\theta^2\right) \quad \ldots \ldots \text{(approx.)} \ldots \quad (19)$$

The lines of flow of energy are determined by the condition that at any point (r_2, θ) the inclination to the

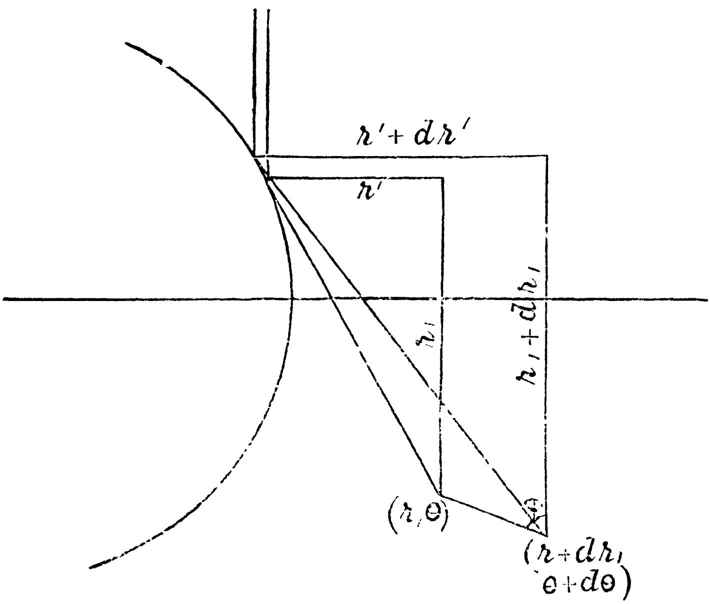


Fig. 2

direct rays is φ, where φ is given by equation (18). From this, we can get the differential equation to the lines of flow in terms of r_2 and θ, or dropping the suffix, in terms of r and θ. It is seen from fig. 2, that

$$\tan\varphi=\frac{dr'-a\theta d\theta}{dr_1-ad\theta}$$

But $r'=r\sin 2\theta=2r\theta$; $r_1=r\cos 2\theta=r$ (approx.)

$$\therefore\ \tan\varphi=\frac{2\,(rd\theta+\theta dr)-a\theta d\theta}{dr-ad\theta}$$

$$\text{or}\ \tan\varphi\left(1-a\frac{d\theta}{dr}\right)=2\theta+(2r-a\theta)\frac{d\theta}{dr}. \quad \ldots \quad \ldots \quad (20)$$

From (18) and (20), we get

$$\frac{d\theta}{dr}\,(2r-a\theta)+2\theta=\left(1-a\,\frac{d\theta}{dr}\right)\frac{2K\theta\left(K-\cos\frac{n}{c}\,2r\theta^2\right)}{1+K^2-2K\cos\frac{n}{c}\,2r\theta^2}$$

which on reduction becomes

$$\frac{d\theta}{dr}=-\frac{\theta}{r}\cdot\frac{1-K\cos\frac{n}{c}2r\theta^2}{1-2K\cos\frac{n}{c}\,2r\theta^2}\ . \quad \ldots \quad \ldots \quad (21)$$

Equation (21) may also be written

$$d\,(r\theta)-\frac{K}{2\theta}\cdot\frac{c}{n}.\cos\psi\ d\psi=0 \quad \ldots \quad \ldots \quad (22)$$

where $\psi=\frac{n}{c}\,2r\theta^2$.

In the immediate neighbourhood of a point, we can regard $\frac{K}{\theta}$ which is equal to $\left\{\frac{a}{\theta\,(2r+a\theta)}\right\}^{\frac{1}{2}}$ as constant since its variation with θ and r will be small compared with the periodic part. On integrating (22), we get

$$r\theta-\left(\frac{K}{2\theta}\right)\frac{c}{n}\sin\psi=\text{const.} \quad \ldots \quad \ldots \quad (23)$$

which determines the shape of the lines of flow in the immediate neighbourhood of a point. The points of intersection of these curves with the loci of maxima and minima of illumination ($\psi=m\pi$), are given by the equation

$$r\theta=\text{const.} \quad \ldots \quad \ldots \quad \ldots \quad (24)$$

This gives the "mean lines of flow" about which energy "crinkles" down. They are shown in Plate II (thin lines). We find that so long as θ is not very large, these curves are inclined to the direct rays at angles smaller than those corresponding to the maxima and minima loci. If we imagine the latter set of curves as forming successive bright and dark tubes, energy will flow down across the tubes, its direction being periodically shifted such that it tends to flow along the bright tubes and to cut across dark tubes. The shift in its direction goes through one complete cycle, as the energy passes from one dark tube, to the next dark tube, or from one bright tube to the next, so that the 'Wave-length' of a crinkle in the neighbourhood of a point (r,θ) may be determined by finding the distance, along the curve $r\theta=$const., between two successive points of intersection of that curve and the family of curves $r\theta^2=\frac{m\lambda}{2}$ (the loci of minima of illumination). Thus

$$r\theta^2=\frac{m\lambda}{2}\,;\ r\theta=C$$

giving $\theta=\frac{m\lambda}{2C}$ or $\delta\theta=\frac{\lambda}{2C}$

if $\delta\theta$ be the difference in the θ-co-ordinates between two successive points of intersection. Also if σ be the arc measured along the curve $r\theta=C$, we have from equation (20)

$$\left(\frac{d\sigma}{d\theta}\right)^2=\left\{(2r-a\theta)+2\theta\frac{dr}{d\theta}\right\}^2+\left\{\frac{dr}{d\theta}-a\right\}^2 \quad \ldots \quad (25)$$

Along the curve $r\theta=C$, $\frac{dr}{d\theta}=-\frac{r}{\theta}$.

Hence from (25) $\left(\frac{d\sigma}{d\theta}\right)^2=a^2+\frac{r^2}{\theta^2}+\frac{2ar}{\theta}$ approximately.

$$\frac{d\sigma}{d\theta}=a+\frac{r}{\theta}=a+\frac{C}{\theta^2}.$$

If l be the "wave-length" of a crinkle,

$$l=\left(a+\frac{C}{\theta^2}\right)\delta\theta=\left(a+\frac{C}{\theta^2}\right)\frac{\lambda}{2C} \quad \text{approx.}$$

$$=\frac{a\lambda}{2C}+\frac{\lambda}{2\theta^2} \quad .. \quad ... \quad ... \quad (26).$$

C being the same, l increases as θ decreases, the rate of increase getting larger as the absolute value of θ diminishes; $l=\infty$ when $\theta=0$. Again as we move away from the cylinder to the right, both C and θ increase, so that l decreases. These points are brought out in Plate III.

Turning back to equation (23), the lines of flow near the point $r_1\theta_1$ are given by

$$r\theta=C-\frac{K_1}{\theta_1}\frac{\lambda}{4\pi}\sin\psi.$$

The curves will obviously lie between the curves

$$r\theta=C\pm\frac{K_1}{\theta_1}\frac{\lambda}{4\pi}.$$

The deviation from the mean line $r\theta=C$ is proportional to

$$\frac{K_1}{\theta_1}=\left\{\frac{a}{\theta\,(2r+a\theta_1)}\right\}^{\frac{1}{2}}$$

As either r or θ increases, this will decrease. The "amplitude" of these crinkles therefore gets smaller and smaller as r and θ increase, and the crinkles vanish at sufficiently large distances from the cylinder.

The shape of the lines of flow very near the surface of the cylinder is of special interest. The energy which comes crinkling down successive loci of maxima and minima of illumination, when it reaches the first maximum, flows down in a smooth curve which will

meet the mean line of flow only at infinity. The energy does not crinkle along after it has crossed the first maximum of illumination.

It is thus seen that the introduction of a perfectly reflecting cylinder into a field through which plane light waves are passing, has the effect of (1) altering the general direction of flow of energy, and (2) giving a crinkled microscopic structure to the energy current at any point. But we have still to seek an explanation as to how a flow of energy in the manner described above leads to the actual distribution of maxima and minima of illumination in the field. The current of energy at any point is by (19)

$$\overline{S}=\frac{c}{8\pi}\left(1-2K\cos\frac{n}{c}2r\theta^2+K^2\right)$$

and this varies from point to point along each line of flow, being maximum and minimum respectively where it cuts successive curves $2r\theta^2=m\lambda/2$. This variation of the current of energy along its own line of flow can be explained only as due to the change in cross-section of the tube of flow formed by two lines of flow close to each other. The conception of energy as flowing through tubes must therefore give us a better idea of what happens in the field.

The curves which are at every point normal to the lines of flow, *i.e.*, the curves analogous to equipotential curves, can easily be obtained. For these curves,

$$\tan\varphi'=-\frac{1-2K\cos\frac{n}{c}2r\theta^2+K^2}{2\theta\left(K^2-K\cos\frac{n}{c}2r\theta^2\right)} \qquad \text{[cp. } eqn. \text{ (2)]}$$

The differential equation in terms of θ and r is found to be

$$(dr-ad\theta)+\frac{2K}{1+K^2}\cos\frac{n}{c}2r\theta^2\left[(a-2r\theta)\,d\theta-dr\right]=0.$$

In the immediate neighbourhood of a point, we can as before leave out all variations other than the periodic one, and integrate. Then we get

$$r-a\theta+\frac{2K_1}{1+K_1^2}\sin\frac{n}{c}2r\theta^2\left[\frac{a-2r_1\theta_1}{4r\theta\frac{n}{c}}-\frac{1}{2\theta^2\frac{n}{c}}\right]=\text{const.} \quad (27)$$

which cuts the successive loci of maxima and minima of illumination at points lying on the curve

$$r-a\theta=\text{const.} \quad \ldots \quad \ldots \quad \ldots \quad (28)$$

which is therefore the mean curve about which the actual curves crinkle round. In the rectangular co-ordinates (x, y), equation (28) becomes

$$y=\text{const.}$$

i.e., the mean curves are straight lines parallel to the to the x-axis. The curves are shown in Plate IV, in relation to the lines of flow and to the loci of minimum illumination. Suppose one of these curves cuts two successive minima loci at points A and B. Then by equation (27), there is one complete crinkle between A and B. Consider the tube of flow bounded by the lines of flow which pass through A and B. Since the flow of energy should be everywhere normal to the wavy curve AOB, energy is concentrated in the right half of the tube and 'rarefied' in the left half. If we draw the line of flow passing through a point O, midway between A and B, we see that we can conceive of the tube AB as made up of two tubes each of which widens and contracts periodically, and one of which is so shifted relatively to the other, that the broadened part of one falls by

the side of the narrow part of the other. We see also from Plate IV, that the contracted parts of successive tubes lie along the loci of max. illumination.

We may now take into account the diffraction at the edge of the cylinder and obtain the correction to our results necessary for points below the plane $y=0$. Using Sommerfeld's expression as we have done before, the electric intensity at a point P′ (fig. 1.) due to this alone is from (6)

$$\frac{1}{4\pi}\sqrt{\frac{\lambda}{r'}}\cos\left\{\frac{n}{c}(r'-ct)+\frac{\pi}{4}\right\}\left\{1-\frac{1}{\sin\frac{\alpha}{2}}\right\}$$

$$=-\frac{1}{2\pi\alpha}\sqrt{\frac{\lambda}{r'}}\cos\left\{\frac{n}{c}(r'-ct)+\frac{\pi}{4}\right\}$$

since α is small; $r'=\mathrm{P'O}$.

Let $\mathrm{P'Q}=r$, and $\mathrm{P'M'}=r_1$.

Then $r'=(r_1-a\theta)\sec\alpha=(r_1-a\theta)\sec 2\theta$

$$=-a\theta+r_1(1+2\theta^2) \quad \text{approximately.}$$

$$\therefore r'+a\theta=r_1(1+2\theta^2).$$

$$\alpha=\frac{2r\theta}{r-a\theta}.$$

If E and H be the resultant electric and magnetic intensities at P′,

$$\mathrm{E}=\cos n\left(t-\frac{r_1}{c}\right)-\mathrm{K}\cos n\left(t-\frac{r}{c}\right)$$

$$-\frac{1}{2\pi\alpha}\sqrt{\frac{\lambda}{r'}}\cos\left\{n\left(t-\frac{r'+a\theta}{c}\right)-\frac{\pi}{4}\right\}$$

and $\mathrm{H}=\cos n\left(t-\frac{r_1}{c}\right)-\mathrm{K}\cos n\left(t-\frac{r}{c}\right)$

$$-\frac{1}{2\pi\alpha}\sqrt{\frac{\lambda}{r'}}\cos\left\{n\left(t-\frac{r'+a\theta}{c}\right)-\frac{\pi}{4}\right\}$$

If $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$, be unit vectors measured along r_1, r and r' respectively, the time-mean of the Flow of energy is found to be given by

$$\frac{8\pi\bar{S}}{c}=\mathbf{k}_1\left[1-K\cos\frac{n}{c}2r\theta^2-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)\right]$$
$$+\mathbf{k}_2\left[K^2-K\cos\frac{n}{c}2r\theta^2+KK'\cos\frac{\pi}{4}\right]$$
$$+\mathbf{k}_3\left[K'^2-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)+KK'\cos\frac{\pi}{4}\right]$$

K′ being written for $\frac{1}{2\pi\alpha}\sqrt{\frac{\lambda}{r}}$.

Resolving the vectors along and perpendicular to the direction of the direct rays, we get

$$\left.\begin{aligned}\frac{8\pi}{c}\bar{S}_x&=1+K^2+K'^2-2K\cos\frac{n}{c}2r\theta^2-2K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)\\&\qquad+2KK'\cos\frac{\pi}{4}.\\\frac{8\pi}{c}\bar{S}_y&=2\theta\left\{-K\cos\frac{n}{c}2r\theta^2-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)\right.\\&\qquad\left.+2KK'\cos\frac{\pi}{4}+K^2+K'^2\right\}\end{aligned}\right\}\ 29$$

where θ^2 is neglected in comparison with unity and α and θ are considered to be the same in the small term $\bar{S}_y$. Since K, K′ are each small in the present problem, terms involving their products and squares can be neglected. The expression for $\tan\varphi$ may then be written

$$\tan\varphi=\frac{\bar{S}_y}{\bar{S}_x}=\frac{2\theta\left\{-K\cos\frac{n}{c}2r\theta^2-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)\right\}}{1-2K\cos\frac{n}{c}2r\theta^2-2K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)}\qquad(30)$$

From equation (20)

$$\frac{d\theta}{dr}(2r+a\theta)+2\theta=\left(1-a\frac{d\theta}{dr}\right)\tan\varphi$$

and (30) becomes on reduction

$$\frac{d\theta}{dr} = -\frac{\theta}{r} \cdot \frac{1 - \mathrm{K} \cos \frac{n}{c} 2r\theta^2 - \mathrm{K}' \cos \left(\frac{n}{c} 2r\theta^2 + \frac{\pi}{4}\right)}{1 - 2\mathrm{K} \cos \frac{n}{c} 2r\theta^2 - 2\mathrm{K}' \cos \left(\frac{n}{c} 2r\theta^2 + \frac{\pi}{4}\right)} \quad \ldots (31)$$

Now $\mathrm{K} \cos \frac{n}{c} 2r\theta^2 + \mathrm{K}' \cos \left(\frac{n}{c} 2r\theta^2 + \frac{\pi}{4}\right)$

$$= \mathrm{D} \cos \left(\frac{n}{c} 2r\theta^2 + \epsilon\right)$$

if $\mathrm{D}^2 = (\mathrm{K} + \mathrm{K}'/\sqrt{2})^2 + \frac{\mathrm{K}'^2}{2} = \mathrm{K}^2 + \mathrm{K}'^2 + \mathrm{K}\mathrm{K}'.\sqrt{2}$

and $\tan \epsilon = \frac{\mathrm{K}'}{\mathrm{K}' + \mathrm{K}\sqrt{2}}.$

Then (30) may be written

$$\frac{d\theta}{dr} = -\frac{\theta}{r} \frac{1 - \mathrm{D} \cos \left(\frac{n}{c} 2r\theta^2 + \epsilon\right)}{1 - 2\,\mathrm{D} \cos \left(\frac{n}{c} 2r\theta^2 + \epsilon\right)}. \quad \ldots (32)$$

In the neighbourhood of any point, D and ϵ can be regarded as constant and equation (32) integrated.

$$r\theta = \mathrm{C} - \frac{\mathrm{D}_1}{\theta_1} \sin \left(\frac{n}{c} 2r\theta^2 + \epsilon\right)$$

The "mean lines of flow" of energy are still given by

$$r\theta = \mathrm{C}.$$

but the actual lines of flow which wind about them cut them along the curves

$$\frac{n}{c} 2r\theta^2 + \epsilon = m\pi \quad \ldots \quad \ldots (33)$$

instead of the curves $\frac{n}{c} 2r\theta^2 = m\pi$. It may be noted that it is equation (33) that determines the position of the maxima and minima of illumination when the effect of diffraction is also taken into account, so that the points of intersection of the lines of flow with the loci of points of max. and min. illumination still lie on the "mean lines of flow."

If the squares and products of K, are not neglected, it can be shown that the mean lines are given by the equation

$$rd\theta\,(1+K'^2+\sqrt{2}\,KK')+\theta dr=0.$$

$$\text{or}\quad r\theta^{1+\alpha}=\text{const.}$$

$$\text{where}\quad \alpha=K'^2+KK.'\sqrt{2}$$

It will be interesting finally to deduce the results for the case of diffraction at a straight edge from the above investigation. Putting $a=o$, K becomes zero also. We have then directly from equations (29)

$$\tan\varphi=\frac{2\theta\left\{K'^2-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)\right\}}{1+K'^2-2K'\cos\left\{\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right\}}$$

$$\text{and}\quad \frac{d\theta}{dr}=-\frac{\theta}{r}\cdot\frac{1-K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)}{1-2K'\cos\left(\frac{n}{c}2r\theta^2+\frac{\pi}{4}\right)}$$

an expression very similar to (21).
The "mean lines of flow" are given by $r\theta=$const. or in the rectangular co-ordinates used, by $x=$const. They are straight lines parallel to the Y-axis, the "mean direction" of energy flow being apparently not altered by the presence of the edge. The actual lines of flow cut the successive loci of points of max. and min. illumination (*i. e.*, the curves $2r\theta^2+\frac{\lambda}{8}=m\frac{\lambda}{2}$) at points which lie along the mean lines of flow. The shape of these lines of flow in the diffraction field due to a straight edge is indicated in the figure in Plate V, which has been drawn for $\lambda=0.5$ inch for convenience of representation.

§ 6. *Summary and Conclusion.*

The present paper deals with the distribution and flow of energy in the immediate neighbourhood of a perfectly reflecting cylinder on which plane light waves are grazingly incident in a direction at right angles to its axis. The following are the principal results which are indicated by theory, and have been verified by photometric study of the field.

(*a*) The positions of the maxima and minima of illumination are determined by eliminating θ from the pair of equations,

$$2y\theta+3a\theta^2/2=x\,;\;\; 2\theta^2\,(y+a\theta)=m\lambda/2$$

or from the pair of equations

$$2y\theta+3a\theta^2/2=x\,;\;\; 2\theta^2\,(y+a\theta)=m\lambda/2-\epsilon\lambda/2\pi$$

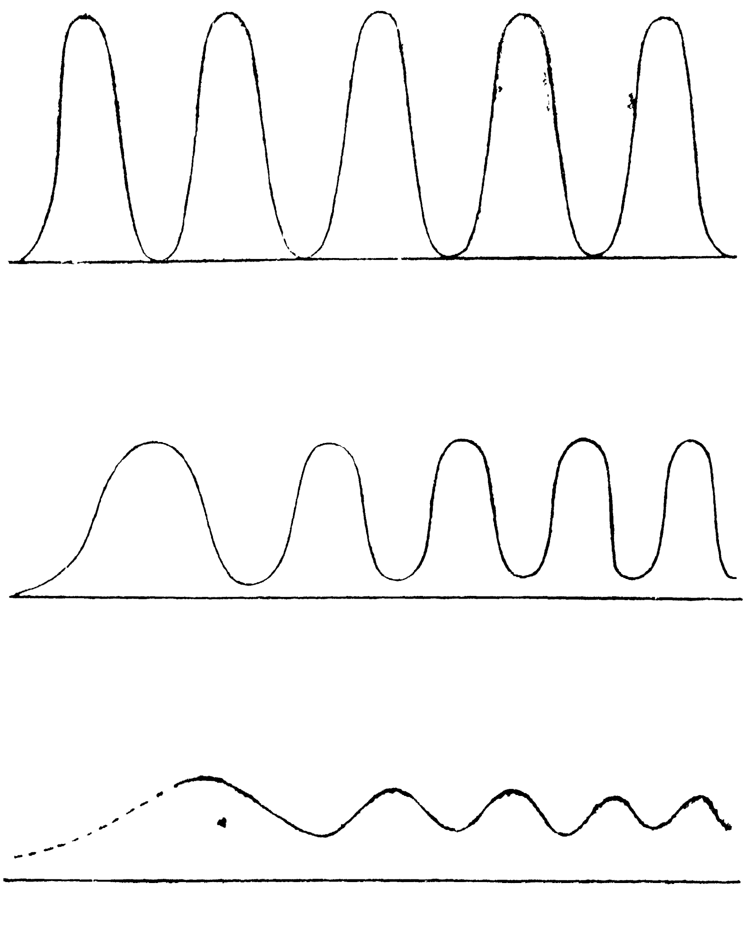
according as the plane of observation is in front of the cylindrical "edge" or behind it. x, y are the co-ordinates of any point, the origin being the "edge" of the cylinder. ϵ is a small angle which for large values of y becomes equal to $\pi/4$.

(*b*) The visibility of the fringes varies in an interesting manner with the position of the part of the field under observation. It is practically constant over the entire plane of observation when this coincides with the plane passing through the "edge," but falls off when it is moved further away from the source of light, the decrease being greatest for the regions farthest from the surface. When the part of the field under observation is between the "edge" and the source of light, the visibility of the fringes reaches the maximum value at the surface of the cylinder, falling off slowly as we recede from it.

(c) The loci of maxima and minima of illumination are given by $r\theta^2 = m\lambda/4$ and the "mean lines of flow" of energy are given by $r\theta$=const. and are for small values of θ, less inclined to the direction of the incident rays than the former set of curves. The actual lines of flow crinkle about these mean lines; the "wave-length" of the crinkles increases as we move along the direction of the incident rays, and decreases as we move in a direction at right angles to it, away from the cylinder. The "amplitude" of the crinkles decreases as r and θ increase, and vanishes at sufficiently large distances from the cylinder. A good conception of the actual phenomena is obtained, if we imagine energy as flowing through tubes which widen and contract periodically, the widened parts of successive tubes lying on the loci of minimum illumination, and the contracted parts on the loci of maximum illumination (see Plate IV). When the radius of the cylinder is very small, the results obtained are practically identical with those obtained in the case of diffraction by a straight edge.

No reference has so far been made to the phenomena noticed within the region of the geometrical shadow of the cylinder. The writer has made some preliminary observations on this subject, and hopes on a suitable opportunity to continue the work, which might prove of interest in relation to the general problem of the diffraction of electro-magnetic waves by cylindrical or spherical surfaces of large radius.

October, 1917.

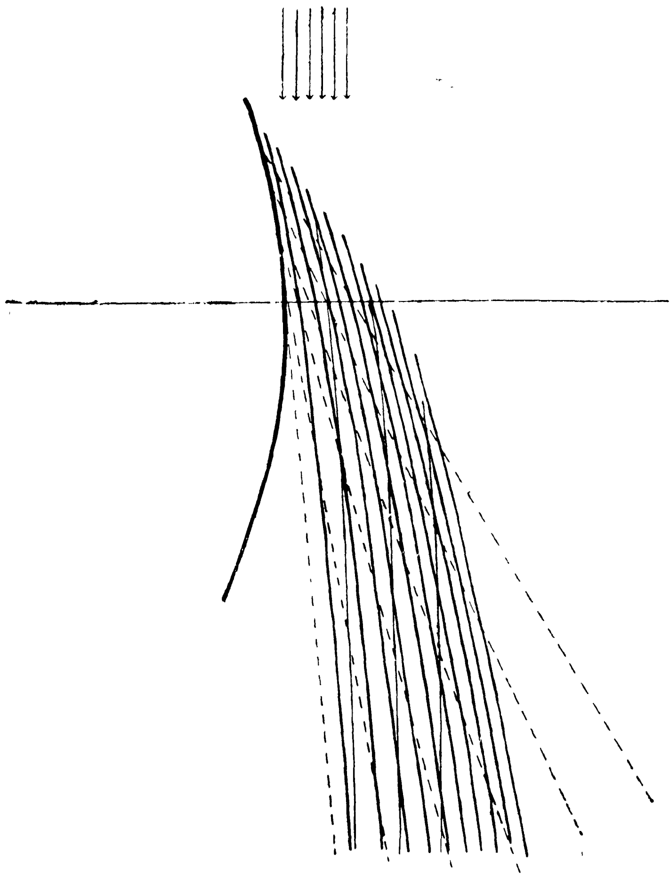


(a)

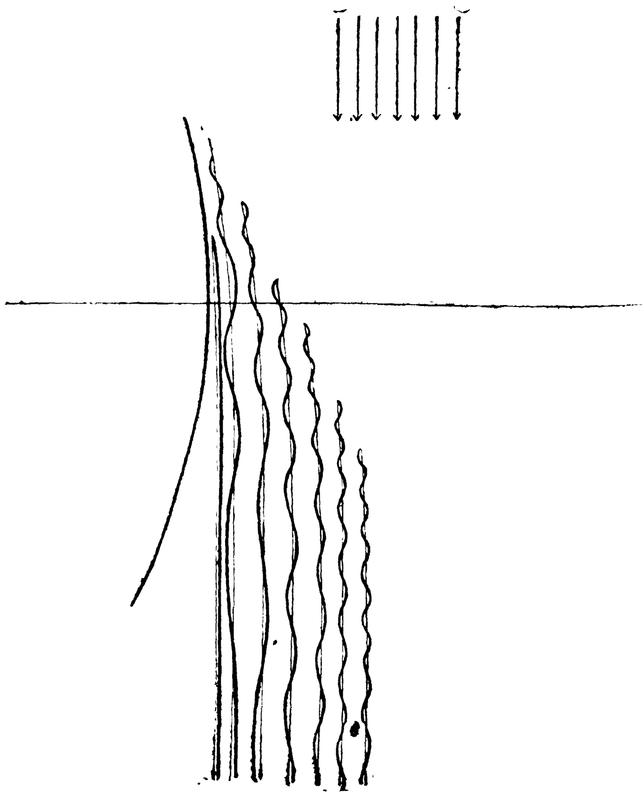
(b)

(c)

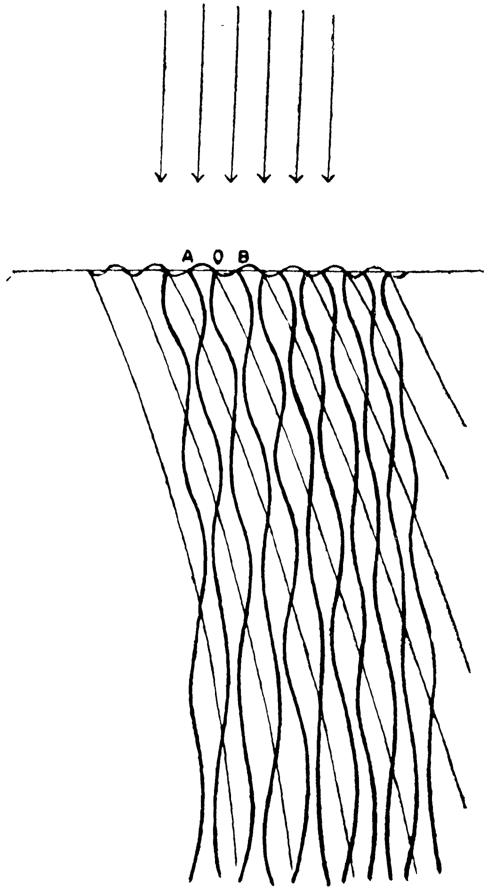
Illumination Curves.



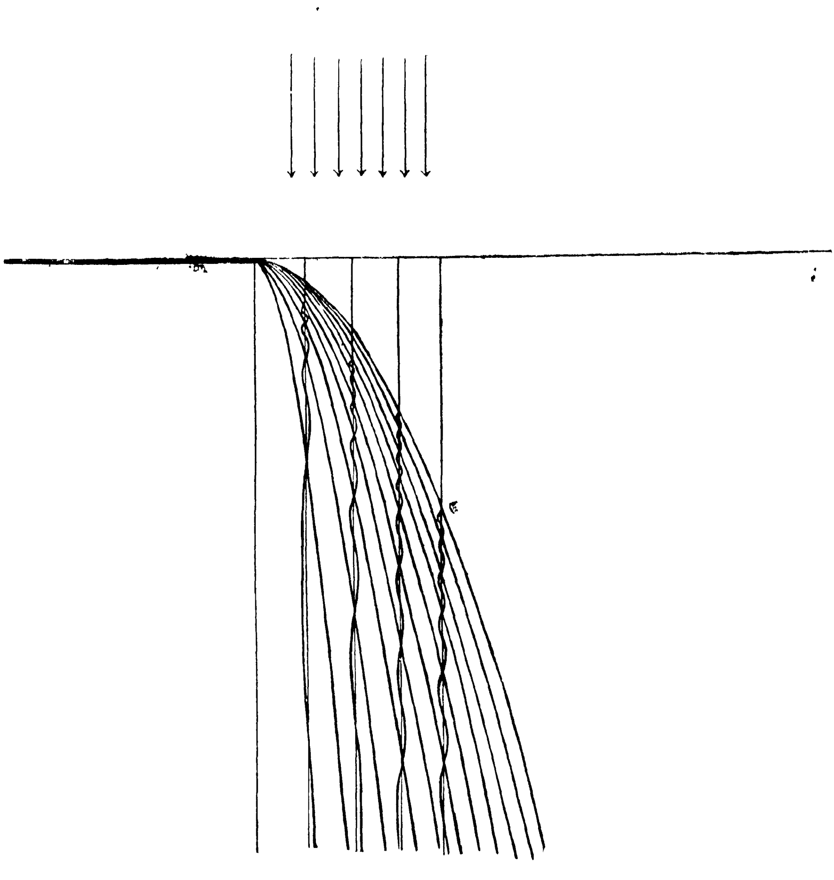
Heavy lines represent the loci of minimum illumination, thin lines the "mean lines of flow" of energy, and dotted lines ther eflected rays.



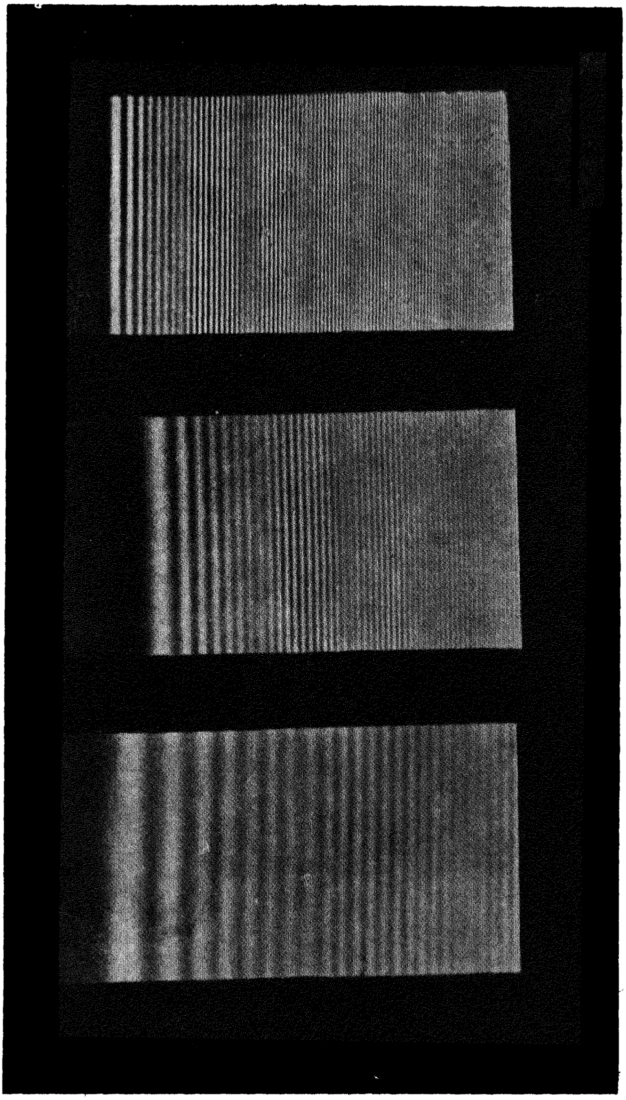
Lines of flow of energy in different parts of the field.



Microscopic structure of the field.



Lines of energy flow in the field due to diffraction
at a straight edge.


(a)

(b)

(c)

Illustrating the Interferences in the Field surrounding a Reflecting Cylinder, and the Decrease in the Visibility of the Fringes with Increasing Distances from the Cylinder.

PROCEEDINGS

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Vol. III. PART VI.

On Resonance Radiation and the Quantum Theory.*

BY T. K. CHINMAYANANDAM, B.A. (HONS.)

§ 1. *Introduction.*

The most fascinating problem, and the problem that is engaging the attention of the most eminent scientists of the world at the present day, is the problem of atomic structure. As has been expected for over a long time, the study of the radiation from the atom seems to be the best, and perhaps the only, clue to this problem; and already, as we know, the recent developments in the study of X-rays, and other high frequency radiations, have thrown quite a flood of light into this sub-atomic world. But there seems to be one difficulty, that crops up and mars our progress; if we knew the nature of radiation completely, our way would be easy in solving the problem of atomic structure. But some phenomena have come to light, such as the emission of electrons by X-rays, or ultra-violet rays, which seem to defy all attempts at an explanation on the classical spreading-wave

* Read at the Annual Science Convention, 23rd November, 1917.

theory of radiation. To explain these phenomena, which grow larger in number every day, the theory of radiation has to be entirely recast, and one such attempt and certainly the most important and promising attempt at such a recasting, is the Quantum theory of radiation. Thus the present day position comes out to be that these two problems are closely intertwined, and so are the solutions of those problems; and any promising attempt at the solution of either must be in very close relation with the other.

The Quantum theory of radiation postulates a discontinuity in the absorption and emission of radiations by a substance, and suggests, in fact, that the absorption or emission of a mono-chromatic radiation of frequency ν can take place only in discrete bundles or Quanta as they are called, of energy of amount $h\nu$ where h is Plank's universal constant. In a series of papers in the Philosophical Magazine for 1913, Dr. Bohr has applied this theory to develop a conception of atomic structure, and has shown how the laws of spectral series can be accounted for in the case of Hydrogen, Helium, and also in a general way for other elements. He assumes an atomic model suggested by Sir E. Rutherford, *viz.*, a system with a nucleus of extremely small linear dimensions, and of posititive charge Ne (where N is the atomic number of the element and e the electronic charge) and N electrons revolving in concentric rings round the nucleus. Radiation is due to the reformation of a system, which has lost one or more electrons. This binding of the electrons, Bohr assumes, cannot take place in a continuous manner, but in a series of sudden

discontinuous jumps. If the orbits are for simplicity considered to be circular, his main assumption may be regarded as an atomicity of angular momentum, that is to say, the angular momentum of the electron must always be an exact multiple of $\frac{h}{2\pi}$ where h is Plank's constant. The orbits which satisfy this condition are assumed to be non-radiating orbits, and the electron is supposed to emit a homogeneous radiation in passing from one such orbit to another, or from one "Stationary State" to another as they are called. If W_1, W_2 be the energy of the electrons in two such orbits, it can be shown that the amount of energy emitted $= W_2 - W_1$; and this Bohr equates to $h\nu$ where ν is the frequency of the radiation. In a simple case like Hydrogen where there is only one electron, W_1, W_2 can be easily calculated on the principles of ordinary mechanics; Bohr has thus got the formula

$$V = K\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$$

where n_1, n_2 are integers and $K = \frac{2\pi^2 me^4}{h^3}$. This is of course the Balmer series for Hydrogen, and it may be pointed out that the calculated value of K agrees very closely with the observed value of the Rydberg constant, an agreement on which, in fact, depends much of the success of Bohr's theory. Bohr has not considered, in any great detail, the case of other elements, where the atom has a number of electrons, the case being complicated by the fact that the other electrons will have an effect, besides the nucleus, on the radiating electron. But he has suggested that in the permanent configuration of the atom, or

the configuration of maximum energy, the electrons will all be arranged in a few concentric rings round the nucleus. This is the broad outline of Bohr's theory of spectral series. It may also be pointed out, that Sommerfeld has in a recent paper in the Annalen Der Physik for 1916 has carried the theory further and has shown, how by a consideration of the ellipticity of some of the orbits of the radiating electron, we can explain the doublet and triplet structure of the lines in the spectral series of the elements.

It appeared to me a very important and fascinating problem, to try and apply the foregoing ideas, to the phenomena of Resonance Radiation discovered by Prof. R. W. Wood. The ideas developed by Bohr apply naturally to stimulation of the substance by electric discharge through its vapour; and as Prof. Wood remarked soon after his discovery of the phenomena, we have in Resonance Radiation, an entirely new method of stimulating a substance to emit radiation, and it would be highly interesting to consider whether Bohr's ideas would apply *en bloc* to this case as well. Some peculiar qualitative features of the phenomena, such for example, as the transformation of the Resonance spectrum into a band spectrum under certain conditions, seem to promise very much in throwing light on the problem of atomic structure.

§ 2. *On the Law of Spacing of the Resonance Lines.*

In a recent paper* in the Philosophical Magazine an attempt has been made by Dr. Silberstein, to explain the phenomena of Resonance Radiation, on the prin-

* Dr. Silberstin on *Fluorescent vapours and their magneto-optic properties* Phil., Mag., Sept. 1916.

ciples of classical mechanics. Dr. Silberstein considers, that the electron which emits the radiation, is a non-Hookean resonator *i.e.*, a system in which the restitutive force is not simply proportional to the displacement, the case being analogous to that of combinational tones in sound. Dr. Silberstein follows the analogy, and introduces a small term, depending not upon the square as in the case of sound, but upon the p^{th} power of the displacement, where p is nearly but not exactly equal to one, and thus writes his equation of motion as

$$y + n^2 y + \alpha y^p = e^{int}$$

The consequence of this assumption he finds to be, that the Resonance series should be characterized by constant frequency intervals. He gives in his paper a table, prepared from Wood's data, and thinks that his conclusions from the theory are supported by facts. But a critical examination of his own figures shows that the frequency intervals have a most decided tendency to decrease on the long wave-length side. There are indeed some irregularities, but it is probably due to the fact that he works out successive differences. Adopting a method of calculation, in which the effect of experimental errors is better minimised, I have prepared a table from Wood's data* for the frequencies of the components of the Resonance series of Iodine vapour, and I have found that it is not the frequencies themselves, but their square roots, that have constant intervals in this series.

* Wood. Phil. Mag., **24**, p. 684.

TABLE.

1 Serial No. n.	2 Frequency. ν_n	3 $\dfrac{\nu_0 - \nu_n}{n}$	4 $\dfrac{\nu_0^{\frac{1}{2}} - \nu_n^{\frac{1}{2}}}{n}$
	$10^{10}\times$	$10^{10}\times$	$10^{3}\times$
0	54937·5		
1	54279·0	658·5	141·0
2	53646·9	645·3	138·5
3	53013·0	641·5	137·0
4	52386·0	637·8	137·7
5	51759·0	635·7	137·6
6	51144·0	632·3	137·3
7	50523·0	630·7	137·4
8	49911·0	628·2	137·3
9	...	...	...
10	48696·0	624·1	137·2
11	48096·0	621·9	137·1
12	47493·0	620·4	137·2
13	46902·0	618·1	137·2
14	...	...	...
15	45726·0	614·1	137·1
16	45147·0	611·9	137·0
17	44562·0	610·3	137·1
18	43983·0	608·6	137·4
19	43419·0	606·2	136·9
20	42855·0	604·1	136·9

I have shown in columns 3 and 4 the intervals of the frequencies and the intervals of their square roots respectively; the former are by no means constant, decreasing systematically by about 9% down the column, while the latter are, expcept for the first few lines, remarkably constant. The attempt to explain the phenomena, on the principles of classical mechanics is apparently, therefore, not quite successful even as regards the spacing of the Resonance lines, not to mention other aspects of the question not considered by Silberstein. I propose in the present paper to suggest an explanation of the phenomena on the Quantum theory.

§ 3. *On the Theory of the Stationary States.*

It may be pointed out at the very outset, that we cannot account for the law of spacing of the components in the Resonance series, on Bohr's simple theory of spectral series. For the law that is characteristic of his theory, is of the Balmer type, the variable factor being $\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ and the frequency interval between two successive components in the series will be proportional to $\left\{\frac{1}{n_2^2}-\frac{1}{(n_2+1)^2}\right\}=\frac{2}{n_2^3}$ approximately. This quantity varies with n_2, and the series will not represent anything like the resonance series, unless n_2 were as large as 400 or 500, in which case the orbit of the radiating electron must be of dimensions enormously large compared with molecular dimensions, being of the order 10^{-3} cm. It is apparent, therefore, that we must take into account the effect of the other electrons in the system on the radiating electron and consider

in greater detail the theory of the possible frequencies of radiations from an atomic system having a large number of electrons.

Bohr regards Light radiations to be due to electrons falling into a system which has lost one or more electrons from the outer ring. And as in the course of the reformation of the system it is extremely unlikely that two of the falling electrons are at any instant at the same distance from the nucleus, our problem becomes practically equivalent to determining the "stationary states" and the frequencies of the radiations of an electron in a system consisting of a few electrons revolving one in each ring round the rest of the molecular system. Let us also assume that any one of the electrons, not necessarily the outermost one, has a series of "stationary states" throughout the system, by passage from one to another of which, it can absorb or emit radiation of appropriate frequency.

On these general assumptions, we can derive a formula for the frequencies of the possible radiations from the system. Leaving out the radiating electron itself from reckoning, let us suppose that it lies at any instant between the orbits of the $(\tau_0-1)^{\text{th}}$ and the τ_0^{th} electrons (counted from the outer surface of the system). Then since an electron revolving in a circle, produces very little effect at a point inside its orbit, while for a point outside, the effect is nearly the same, as if it were placed at the centre of its orbit, the radial force on the electron, may be supposed to be due to an equivalent nucleus of charge Se where

$$S=\tau_0+\phi(r) \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$\phi(r)$ being the correction factor, which is a function

of r the radius of the orbit. The function will be definite, if the configuration of the other electrons is given. The force on the electron may hence be written

$$F=\frac{S}{r^2}e^2 \qquad \ldots \qquad \ldots \quad (2)$$

Let v be the velocity of the electron in its orbit. Then

$$\frac{mv^2}{r}=F=\frac{Se^2}{r^2} \qquad \ldots \qquad \ldots \qquad \ldots \quad (3)$$

and since the angular momentum of the electron is a multiple of $\frac{h}{2\pi}$, $mvr=\frac{\tau h}{2\pi}$, where τ is an integer. From these equations, we get,

$$r=\frac{\tau^2 h^2}{4\pi^2 m}\cdot\frac{1}{Se^2}=\frac{k\tau^2}{S} \text{ (say)}. \qquad \ldots \quad (4)$$

If W be the energy of the electron in any of its "stationary states"

$$W=\tfrac{1}{2}mv^2=\frac{2\pi^2 e^4 m}{h^2}\cdot\frac{S^2}{\tau^2} \qquad \ldots \quad (5)$$

so that the possible frequencies of the radiations from the system are given by

$$\nu=\frac{2\pi^2 e^4 m}{h^3}\left\{\frac{S_1^2}{\tau_1^2}-\frac{S_2^2}{\tau_2^2}\right\} \qquad \ldots \qquad \ldots \quad (6)$$

Even without knowing the exact nature of the function $\phi(r)$ in equation (1), it is obvious that the quantity S will increase as r increases, for the repulsion of the inner electrons becomes less, and that of the outer increases. Hence it is evident that, since

$$\frac{S_{\tau_2}}{\tau_2^2}-\frac{S_{\tau_2+1}}{(\tau_2+1)^2}<S_{\tau_2}\left\{\frac{1}{\tau_2^2}-\frac{1}{(\tau_2+1)^2}\right\},$$

closer groups of lines are possible on this theory than on a simple series of the Balmer type. We may now consider what is likely to happen when light of a definite frequency ν excites the system; it will be

absorbed or, in general, will affect the system, if any one of the electrons in the system requires an amount of energy $h\nu$ to pass from any one of its stationary states to any other. Suppose for definiteness, that for the mercury green radiation this condition is satisfied by an electron in a stationary state between the orbits A and B of its neighbours (fig. 1), if it passes to

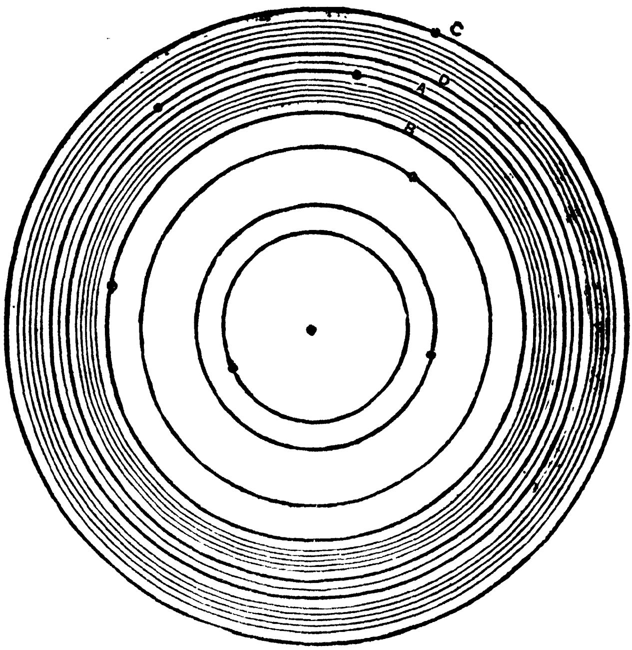

Fig. 1,

a stationary state between C and D orbits, of two other consecutive electrons. Then as soon as the light falls on the system, it will jump from the former to the latter state, absorbing the incident radiation. It then jumps back, emitting radiation. If it jumps exactly to its original orbit, the frequency of the emitted radiation will be the same as that of the incident one; but when it jumped, the configuration must have changed, so

that it is not likely that it jumps exactly to its original path. Let us assume that it jumps to one of the series of stationary orbits; then it is clear, that in the resulting radiation, there will be as many different components as the number of orbits. The frequency intervals of these components will obviously depend upon the difference in the function $\frac{S^2}{\tau^2}$, between the consecutive orbits. To determine the spacing of the lines in the emitted radiation, therefore, we must know more definitely the nature of the function $\frac{S^2}{\tau^2}$. We shall now work out, as an illustrative case, the nature of that func-

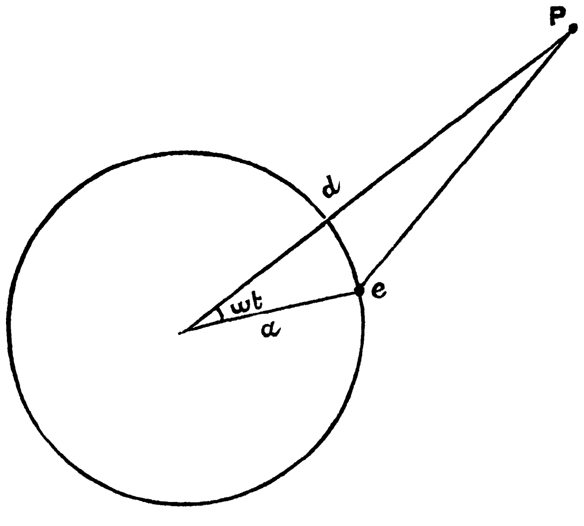

Fig. 2.

tion, on the assumption that the force exerted by a revolving electron is correctly represented by its time-mean value. Thus, if f be the mean force due to an electron revolving in a circle of radius a, at a distance d from its centre,

$$f=\frac{1}{T}\int_0^T \frac{e\,(d-a\cos\omega t)}{(a^2+d^2-2ad\cos\omega t)^{\frac{3}{2}}}\cdot\,\delta t.$$

If $d<a$

$$f=\frac{e}{2\pi}\frac{\partial}{\partial d}\int_0^{2\pi}\frac{1}{a}\left[P_0(\cos\theta)+\frac{d}{a}P_1(\cos\theta)+\ldots\right]\delta\theta$$

$$=-\frac{e}{d^2}\left(\frac{1}{2}\frac{d^3}{a^3}+\frac{9d^5}{16a^5}+\ldots\right)$$

If $d>a$

$$f=\frac{e}{d^2}\left(1+\frac{3}{4}\cdot\frac{a^2}{d^2}+\frac{45}{64}\cdot\frac{a^4}{d^4}+\ldots\right)$$

The function $\phi\ (r)$ becomes

$$\phi(r)=\sum_{\tau_0-1}^{1}\left(\frac{1}{2}\frac{r^3}{a^3}+\frac{9}{16}\cdot\frac{r^5}{a^5}+\ldots\right)$$

$$-\sum_{\tau_0}^{N}\left(\frac{3}{4}\cdot\frac{a^2}{r^2}-\frac{45}{64}\cdot\frac{a^4}{r^4}+\ldots\right).$$

where the summation extends in the first term over all the electrons outside the orbit of the radiating electron, and in the second term over the electrons inside it. Neglecting powers higher than the square, we may write

$$S=\tau_0-\sum_{\tau_0}^{N}\left(\frac{3}{4}\cdot\frac{a^2}{r^2}\right)$$

But from equation (4), $r=\frac{k\tau^2}{S}$, so that

$$S=\tau_0-\sum_{\tau_0}^{N}\frac{3}{4}\cdot\frac{a^2S^2}{k^2\tau^4}.$$

Denote $\sum_{\tau_0}^{N}\frac{3}{4}\cdot\frac{a^2}{k^2}$ by c.

Then $\frac{Sc^2}{\tau^4}+S-\tau_0=0.$

Hence $S=-\frac{\tau^4}{2c}+\left\{\frac{\tau^8}{4c^2}+\frac{\tau_0\tau^4}{c}\right\}^{\frac{1}{2}}$

$$S^2=\frac{\tau_0\tau^4}{c}+\frac{\tau^8}{2c^2}-\frac{\tau^4}{c}\left\{\frac{\tau^8}{4c^2}+\frac{\tau_0\tau^4}{c}\right\}^{\frac{1}{2}}$$

now $c=\Sigma\frac{3}{4}\frac{a^2}{k^2}$ and will be of the order $\Sigma\frac{3}{4}\cdot\frac{\tau_m{}^4}{m^2}$, if τ_m corresponds to the orbit of the m[th] electron, and

unless the electrons in the periphery of the atom are revolving in orbits extremely close to one another, c will hence be smaller than $\frac{\tau^4}{\tau_0^2}$. The first term under the square-root will be larger than the second, and we may write

$$S^2=\frac{\tau_0\tau^4}{c}+\frac{\tau^8}{2c^2}-\frac{\tau^8}{2c^2}\left(1+\frac{2c\tau_0}{\tau^4}-\frac{2c^2\tau_0^2}{\tau^8}+\frac{4c^3\tau_0^3}{\tau^{12}}-\cdots\right)$$

$$=\tau_0^2-\frac{2c\tau_0^3}{\tau^4}+\cdots$$

$$\frac{S^2}{\tau^2}=\frac{\tau_0^2}{\tau^2}-\frac{2c\tau_0^3}{\tau^6}+\cdots=y \text{ (say)}.$$

Now the frequency intervals between two successive components of the series of radiations must be proportional, on the present theory, to the difference in the value of this function y in any two consecutive "stationary states." We can approximately obtain the latter by differentiating y with respect to τ. Thus

$$\frac{dy}{d\tau}=-\frac{2\tau_0^2}{\tau^3}+\frac{12c\tau_0^3}{\tau^7}.$$

Let us reckon from a line in the series which corresponds to the path τ_1 and write for the successive lines $\tau=\tau_1+n$. Then if ν_{n-1}, ν_n be the frequencies of two successive lines in the series of radiations.

$$\frac{1}{K}\left(\nu_{n-1}-\nu_n\right)=\frac{2\tau_0^2}{\tau_1^3}-\frac{12c\tau_0^3}{\tau_1^7}-\frac{n}{\tau_1}\left(\frac{6\tau_0^2}{\tau_1^3}-\frac{84c\tau_0^3}{\tau_1^7}\right)-\frac{n^3}{\tau_1^2}\left(\cdots\right) \quad \cdots \quad \cdots \quad (7)$$

and can be written in the form

$$\nu_{n-1}-\nu_n=\alpha+\beta n+\gamma n^2+\ldots .$$

If the coefficient α, β, γ etc. are all exactly zero, the resonance series will be characterized by constant frequency intervals. It does not seem possible, without

making further assumptions to determine their magnitude absolutely. But though it is unlikely that α, β, γ, all vanish, it can be seen that the successive coefficients will decrease rapidly. In the case of Iodine vapour, it was pointed out in the previous section that $\nu_{n-1}^{\frac{1}{2}} - \nu_n^{\frac{1}{2}}$ seemed to be constant. This relation is equivalant to

$$\nu_{n-1} - \nu_n = 2\nu_0\delta - 2n\delta^2,$$

where $\delta = \nu_{n-1}^{\frac{1}{2}} - \nu_n^{\frac{1}{2}}$. Thus $\nu_{n-1} - \nu_n$ is of the form $(\alpha + \beta n)$. It is also possible to show that the quantities α, β given by equation (7) are of the right order. Thus in the case of Iodine vapour $\frac{\alpha}{K}$ is about 2×10^{-3} and $\frac{\beta}{K}$ about 10^{-5}. Hence we shall have

$$\frac{2\tau_0^2}{\tau_1^3} - \frac{12c\tau_0^3}{\tau_1^7} = 2 \times 10^{-3}.$$

$$\frac{1}{\tau_1}\left\{\frac{6\tau_0^2}{\tau_1^3} - \frac{84c\tau_0^3}{\tau_1^7}\right\} = 10^{-5}$$

Putting $\tau_0 = 2$, we get τ_1 to be about 13, and the diameter of the orbit of the electron will be of the order of 10^{-6} cm., which does not seem improbable, when account is taken of the fact that the vapour must be at a very low pressure to emit Resonance radiation.

It may be pointed out here, however, that since the equation $\nu_{n-1} - \nu_n = \alpha + \beta n$ is more general than the equation $\nu_{n-1}^{\frac{1}{2}} - \nu_n^{\frac{1}{2}} = \delta$, it seems only accidental, on the present hypothesis, that the latter formula holds very approximately in the case of Iodine vapour. In the case of Sodium vapour it has been found by the writer, that while there is no approach to constant frequency intervals, even the expression $\nu_{n-1}^{\frac{1}{2}} - \nu_n^{\frac{1}{2}}$ gives

a systematic deviation on one side, so that this form has perhaps no special significance.

One point still remains to be noticed. In a Resonance series ordinarily as many as 20 lines are observed, and we cannot certainly assume that there are as many orbits between two consecutive electrons of the system, to which it can jump. This difficuity is easily got over, if we assume that it need not jump from the same orbit every time, but from one of a series of orbits between C and D (fig. 1). It is obvious, then, that we can account for as many as 25 lines in the resonance series with only 5 orbits in each series; suppose, for example, the interval of the function $\frac{S^2}{\tau^2}$ is constant over successive orbits in each series, but the interval in one series is 5 times that in the other; then, we shall have 25 lines in the resonance spectrum at constant frequency intervals. It seems at first sight unlikely that the resonance series of Iodine vapour is made up of smaller series patched up like this; for, if it is so formed, the patching up must be very nicely adjusted, so as to make the series indistinguishable from a single continuous series. But certain observations of Wood*, regarding the Resonance radiation of Sodium vapour, seem to bear out the suggestions that have been put forth here. Wood has found that, as we go away from the resonance line, new lines appear, which do not belong to the old series, and new series start from where the old ones leave off. This is exactly what should be expected, if in the above illustration considered, the interval of

* Prof. R. W. Wood. Phil. Mag., **25**, p. 588.

$\frac{S^2}{\tau^2}$ in one series of orbits is not an exact multiple of that in the other series. As a matter of fact, generally only 4 or 5 lines can be made out as forming one continuous series; and the whole resonance spectrum is made up of bits like these. Even in the case of Iodine vapour, a grouping suggested by Wood* from a consideration of the structure of these lines, seems to give additional evidence to the suggestions offered here.

§ 4. *Some Characteristics of Resonance Radiation.*

Coming back to the mechanism of resonance radiation, the main point in the hypothesis suggested here is that soon after the external radiation has begun to excite the system, if not even before, in the permanent configuration of the system itself, the electrons in the periphery of the atom are revolving one in each ring round the nucleus, and one particular electron absorbs and emits light by passing from one of a series of "stationary states" between two consecutive electrons to another series of states between another pair of consecutive electrons. The frequency intervals between successive components in the emitted radiation are proportional to the intervals of the function $\frac{S^2}{\tau^2}$ over consecutive "stationary states" in the same series, and, as is evident from the analysis given in the previous section, they will depend upon the configuration of the other peripheral electrons, both relative to themselves and relative to the nucleus. It is not to be expected, *a priori*, that this configuration will be the

* Wood. Phil. Mag., **26**, p. 841.

same for all the molecular systems, and hence each molecular system may, in general, be expected to give its own Resonance series. We can more easily conceive, therefore, of the system giving a band-spectrum than a line-spectrum. Experimental evidence seems generally to support this conclusion, Resonance spectra being exhibited by very few substances, and by these, only under particular conditions of temperature and pressure ; and they are either destroyed altogether, or give place to the band-spectrum under slight disturbing causes. But the fact that it does occur under some conditions, points to the conclusion that there are some stable or quasi-stable configurations which are characteristic of the substance and hence assumed by the falling electrons in all the systems at once. All configurations very near these quasi-stable configurations lead to these latter configurations, though a configuration very different from them may not do so, the case being perhaps something like that of the configurations that may be assumed by a system of floating magnets.

On this view, we find an easy interpretation of the fact that the resonance spectrum of Iodine vapour, is transformed into a band-spectum, on rarefying the vapour ; that is to say, that the same Iodine vapour, when it is at a lower preasure, gives under the same monochromatic excitation, an almost continuous spectrum, instead of the characteristic line spectrum. Wood*, who discovered this phenomenon, gives, however, a different explanation. He thinks that the band-spectrum is always produced, but is absorbed by the fluorescent gas itself when it is dense. He cites

* Wood. Phil. Mag., Nov. 1913.

as an evidence for this, an experiment tried by him, which was to pass the radiation from the rarefied vapour, through another tube containing cool iodine vapour. He found that the band-spectrum was completely absorbed, the resonance lines alone being left out. I will show presently, that the result of this experiment is not inconsistent with the views I have tried to develop. It may be pointed out, meanwhile, that apart from some objections that may be raised against his conclusions, his hypothesis does not lead us very far, and leaves it for further explanation—why from an almost continuous spectrum, only certain lines should be left out unabsorbed. Wood has indeed realised the difficulty, and has raised the question whether the same molecule emits both the resonance and the band-spectra, or only one, and whether in the vapour there are simultaneously systems emitting the two spectra independently. But the essential point about it seems to me to be, that it does not throw any light on the occurrence of the band-spectrum under apparently totally different conditions. Wood and Frank* have discovered that the resonance spectrum of Iodine vapour is transformed into a band-spectrum by the introduction of the gas Helium at a very low pressure. Indeed, the discovery was prior to the one previously mentioned; and Wood says nothing more on it than that it is due to the collision of the Helium molecules with the Iodine molecules. He regards the phenomena as a new effect of molecular collisions on the radiations from an atomic system, and has left it as a problem for the theoretical

* Wood and Frank. Phil. Mag., Feb. 1911.

physictsts to solve. The problem, so far as I know, has not been solved; but Wood has tried to find out whether the fact that Helium has a small affinity for electrons, has anything to do with its behaviour. The facts that have been observed, may be briefly set forth here and an explanation then suggested. Electro-negative gases, that is, gases which have strong affinity for electrons, completely destroy the fluorescence. Gases which have a weak affinity for electrons, like Helium, transform the line-spectrum into a band-spectrum, but this effect does not vary inversely as the affinity for electrons, for Neon, which has a much smaller affinity for electrons than Helium, shows scarcely so marked an effect as Helium in transforming this spectrum. The explanation is briefly this. Electro-negative gases pull out the outer electrons in the Iodine molecule (which are of course those responsible for the resonance spectrum), pull them either into their own molecules or at least so far away from the nucleus as to destroy the condition of absorption of the incident light. Gases like Helium with less affinity for electrons, do not pull these outer electrons so far as to destroy the absorption of the incident light, but far enough to destroy the quasi-stable configurations described above. Gases with absolutely no affinity for electrons, apparently do not produce any effect on the Iodine molecules or on the radiation from them.

I may now explain why the resonance lines are not absorbed, while the band-spectrum is absorbed * when passed through a tube containing cool Iodine vapour.

* See Wood. Phil. Mag., Nov. 1913, p. 838.

The radiation of the resonance lines depends upon a particular quasi-stable configuration assumed by the system, under the action of the exciting light, and naturally, on our theory, can be absorbed by the system only when in that configuration. On the other hand, the band-spectrum is due to molecules in varying configurations, more or less distributed at random, and the vapour in its ordinary state will also generally contain such systems with no unique configuration for all the molecular systems. It is only to be expected, therefore, that the band-spectrum should be absorbed. This explanation is indeed analogous to that given by Bohr* for the fact that Hydrogen does not exhibit absorption lines corresponding to all its radiation frequencies.

We may now pass on to consider the structure of these resonance lines, and also the companion lines that are found in large number distributed throughout the spectrum. As it has been pointed out, it seems very unlikely that under any conditions the configurations of all the molecular systems are the same, though in the case of certain quasi-stable configurations at least most of the molecules must have the same configurations if the substance can emit a line spectrum. But even in the latter case, one would naturally expect some systems to remain "out of tune," and it is suggested here that the companion lines observed are due to these systems which are "not in tune" with the rest. A great point in favour of this suggestion is that most of these lines are faint in comparison with the other lines, which is just what

* Bohr, Phil. Mag., July 1913.

we should expect, since only a few systems are supposed to be emitting them. Further, even in the other systems, if the adjustment is not perfect we should expect the resonance lines to be not quite homogeneous. Wood has found that the structure of these resonance lines is in fact very complex, the number of components in each line observable seeming to depend only on the resolving power used. He considers this to be due to the complex structure of the exciting mercury green line, but as he himself says, the structure of the resonance lines is much more complex, so that each exciting line gives rise to more than one line in the resonance lines or line-groups, as we may call them. Indeed, some of his observations on the complicated effects of changing the structure of the lines, lead us to doubt whether the phenomena of resonance radiation can ever be satisfactorily explained on the principles of classical mechanics.

Reference may now be made also to the point, in what way, if at all, resonance radiation is simpler than radiation excited by other means. Since we use a mono-chromatic exciter, Wood thought that in resonance excitation, we were, as we may call it, striking a single key in the key-board of the atom; and the comparatively simple structure of the resonance spectrum seemed to give weight to this conjecture. But we now know that the emitted radiation is so simple, only under certain conditions; while, under other conditions, the same mono-chromatic exciter gives rise to a band-spectrum. On the views set forth in this paper, the simplicity of the resonance

spectrum is due not to the nature of the exciter but to the nature of the system, to the fact that it has some quasi-stable configuration of the nature described already. In fact, the assumption of such configurations is necessary, even in the case of electrical excitation; Hick's* four "Sequences," for example, require four such definite configurations.

§ 5. *Röntgen Spectra.*

We may now pass on to consider another set of phenomena, which we may term also resonance radiation; when X-rays fall upon a substance, they excite it to something like resonance, when their frequencies are near certain values characteristic of the substance. The resulting radiation from the substance is termed, as we know, the Characteristic radiations, and consists of at least three series of lines, the K, L and M series as they are called. In an epoch-making discovery, Moseley has shown that the characteristic radiations from different elements were related in a simple manner to their relative positions in the periodic table of elements, and more definitely that the frequencies of the K-Characteristic radiations of the elements are represented by the equation

$$\nu = K(N-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

where N is the atomic number and K is the Rydberg constant for Spectral series. He wrote it in this form to bring out the analogy with the Balmer formula, and tried to interpret the formula on Bohr's theory by supposing that the radiations were due to the vibra-

* Hicks, Proc, Roy. Soc., **83**, p. 226.

tions of a ring of four electrons, immediately surrounding the nucleus. But it has been pointed out by Nicholson * and Bohr †, that this is not the correct interpretation, since we will have to assume that several quanta are emitted at the same time. Ishiwara‡ has pointed out that the lines in the Röntgen spectra can be accounted for, if Bohr's spectral formula be altered to

$$\nu = K\left\{\frac{(N-c_1)^2}{(n_1+\mu_1)^2} - \frac{(N-c_2)^2}{(n_2+\mu_2)^2}\right\}.$$

Remembering that the region of excitation in the molecular system is now the innermost ring of elec-

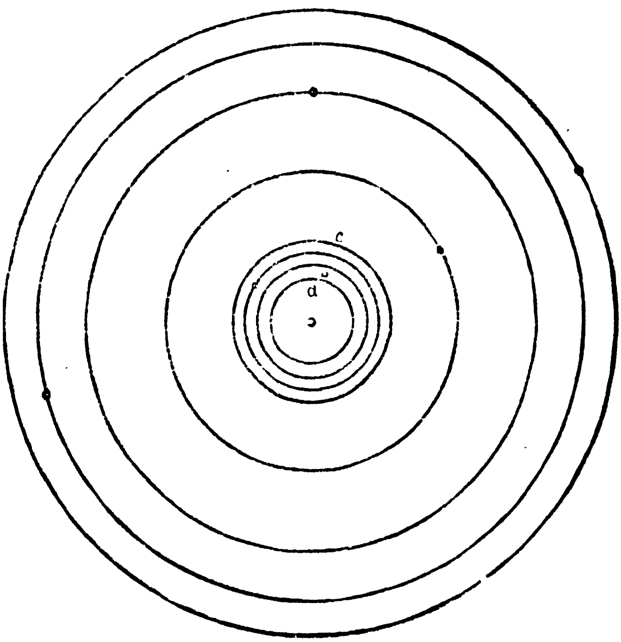

Fig. 3.

* Nicholson, Discussion on the Structure of the Atom, March 19, 1914. Proc. Roy. Soc., vol. 90.

† Bohr, On the structure of the Atom and the Quantum Theory of Radiation, Phil. Mag., Sept. 1915.

‡ Jun Ishiwara, Proc. of the Tokyo Math. Phys. Soc., Ser. 2 vol. 9, p. 160. (July 1917).

trons instead of the outermost, this form can be derived from the general formula obtained in this paper for the frequencies of the radiations from an atomic system, by giving a suitable value to the function $\phi(r)$. A detailed conception of the mechanism of emission of these radiations is also possible. The electron which emits the radiations (very probably the first from the nucleus) is supposed to be in one of its stationary states *b* (fig. 3) inside the orbit of the second electron. Under proper excitation, it is supposed to jump out to an orbit *c* just outside the second electron absorbing energy, and then back again to an orbit near its previous one emitting radiation. The L_α radiation, I suggest, is emitted when it jumps from orbit *c* to orbit *b*; the K_α, from orbit *b* to orbit *a*, and the K_β, from orbit *c* to orbit *a*. Then it evidently follows

$$\nu_1 = \nu_2 + \nu_3$$

if ν_1, ν_2, ν_3, be the frequencies of the K_β, K_α, and L_α radiations of an element, respectively. This is, of course, Kossel's relation. It is also seen, if we assume that the electron is in orbit *b* to begin with, why L_α can be emitted without the K-radiations at the same time being emitted, while K_α cannot be emitted without K_β; and also why the K-radiations are necessarily accompanied by L-radiations. The other lines in the Röntgen spectrum can similarly be accounted for by considering some more orbits of the radiating electron.

The secondary corpuscular radiation, which is found to invariably accompany the emission of Characteristic radiations, may be supposed to be due to the collision

of the radiating electron with the second electron in one of its passages across its orbit, and the consequent dislodgment of the latter. One remarkable result will follow from this supposition, that the velocities of the corpuscular rays should be the same for both the K and L Characteristic radiations. This has really been found to be the case by Barkla and Shearer*, who have noted it as a remarkable fact in view of the general supposition, that the radiations have their origin in two different rings of electrons.

§ 6. *The general law of Spectral Series.*

Before concluding the paper, I will show you how from the atomic structure suggested in this paper a general formula for spectral series can be obtained taking into account all possible regions of excitation. As it has been shown, the frequencies of radiation from an atomic system are given by

$$\nu = K\left\{\frac{S_1^2}{\tau_1^2} - \frac{S_2^2}{\tau_2^2}\right\}$$

Now $S = \tau_0 + \phi(r)$ where r is the radius of the orbit of the radiating electron, and

$$r = \frac{k\tau^2}{S}.$$

so that

$$S = \tau_0 + \phi\left(\frac{k\tau^2}{S}\right),$$

on solving which, we may express S as an explicit function of τ of the form

$$S^2 = \psi_r(\tau)$$

the suffix being introduced to take account of the fact

* Barkla and Shearer, "On the Velocity and electrons expelled by X-rays," Phil. Mag., Dec. 1915.

that the function will change in passing from between one pair of consecutive electrons to another. Thus

$$\nu = K\left\{\frac{\psi_r(\tau_1)}{\tau_1^2} - \frac{\psi_s(\tau_2)}{\tau_2^2}\right\}.$$

This is of the same form as Ritz and Rydberg's general formula, though, as has been indicated, it also represents lines in high frequency spectra.

One point seems worthy of notice. An examination of any general law of spectral series shows us that the functions ψ_r and ψ_s are in actual cases found to be different; in Hicks law of spectral series, for instance, the lines in the spectra are never got from the same "sequence," but from two different sequences, the integral parameter in one of which is given a constant value while that in the other is allowed to vary. This would indicate that the radiations are due to an electron jumping into an orbit between two consecutive electrons in the system from one of a series of orbits outside the two electrons; and it may be remembered that we made the same assumptions in explaining Resonance radiation. It is indeed difficult to explain the fact stated here, if we consider light radiation to be due to the outermost electron, or rather to an electron which remains always the outermost in the system.

In conclusion, it may be pointed out that only the broad outlines of the subject have been touched upon in this paper, so as just to show what light the hypothesis suggested here throws upon the observed phenomena of radiation. The further development, especially with reference to quantitative relationships, is a matter for subsequent investigation.

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Equilibrium between Copper salts and Mercury in presence of Chloridion and Bromidion.

BY JNANENDRA CHANDRA GHOSE, M.Sc.

The replacement of one metal by another in acqueous solutions is capable of exact theoretical treatment. Here the potential difference between the metal and the solution which is given by the equation $-\frac{RT}{nF}\log\frac{C}{c}$ is the determining factor in the reaction. $-\frac{RT}{nF}\log C$ is constant for each metal and is called the normal electrode potential E_n. A metal, *A* replaces, is in equilibrium with, or is replaced by another metal *B* according as

$$(E_n)_A - (E_n)_B > = < \frac{RT}{F}\left[\frac{\log c_a}{n_a} - \frac{\log c_b}{n_b}\right]$$

This conception can also be extended to the action of oxidising agent on metals. $(E_n)_B$ in the above equation means, in this case, the potential difference existing between the oxidising agent and its products of reaction, when the concentration of each of these is normal; and the term $\log C_b$ is $\Sigma n \log C$, *i.e.*, log of the ratio of conc. of the oxidising agent to that of its pro-

duct of reaction. In general cases, the reaction proceeds entirely in one direction for $(E_n)_A - (E_n)_B$ is often large enough to make one of the terms C_a or C_b vanishingly small in comparison with the other.

It is well known that copper salts in presence of hydrochloric acid is reduced by mercury[1]. It has however been found out that in the case of the reaction

$$2CuCl_2 + 2Hg = Hg_2Cl_2 + 2CuCl$$

the cupric salt is not completely reduced to the cuprous state but an equilibrium sets in at a definite measurable concentration of cupric ion. Applying the Law of Mass action to the reaction

$$2C\ddot{u} + 2Hg = H\ddot{g}_2 + 2C\dot{u} \text{ we get}$$

$$K = \frac{[C\dot{C}u]^2}{C_{H\ddot{g}_2} \times [C\ddot{C}u]^2} = \frac{[C\dot{C}u]^2 \times [CCl']^4}{S_1 \times S_2^2} = \left[\frac{[C\dot{C}u] \times [CCl']^2}{\sqrt{S_1} \times S_2}\right]^2$$

$$= \frac{K_1^2}{[\sqrt{S_1} \times S_2]^2}$$

where S_1 is the solubility product of Hg_2Cl_2 and S_2 the solubility product of CuCl.

In the reaction between mercury and cupric salt in presence of bromidion an equilibrium also sets in at a measureable concentration of cupric salt and here also we expect the equation

$$K = \frac{K_2^2}{[\sqrt{S_1'} \times S_2']^2} = \left[\frac{[C\ddot{C}u] \times [CCl']^2}{\sqrt{S_1'} \times S_2'}\right]^2$$

where S'_1 is the solubility product of Hg_2Br_2 and S'_2 that of CuBr, to hold good.

Experimental procedure :—Samples of pure $CuSO_4$, CuBr, KCl and KBr were prepared in the laboratory. $\frac{N}{10}$ solutions of KCl and KBr were prepared, as also

(1). Trans. Chem. Soc. 1911, P. 1415 by Borrar.

stock solutions of $CuSO_4$, $CuCl_2$ and $CuBr_2$ whose strength was measured by means of a standard thio-sulphate solution. A mixture of [$CuCl_2$ – KCl], [$CuBr_2$ – KBr], [$CuSO_4$ – KCl] or [$CuSO_4$ – KBr], as the case may be, of exactly known composition was poured into a stout clean bottle having a capacity of 125 c.c. A suffiicent amount of pure mercury was then put into the bottle and the whole vigorously shaken. In preliminary experiments, the reaction was carried out with air inside the bottles, but as will be shown in Table 2, values of K obtained from several experiments did not agree with one another. It was thought possible that in the presence of an inert gas like CO_2 better results could be obtained. Pure dry CO_2 was, therefore, bubbled through the solution in the bottle for about 15 minutes before mercury was poured in. The bottles were then quickly stoppered with a rubber cork and sealed by means of wax. They were vigorously stirred in an electrically driven shaker for a period of 2½ to 3½ hours. The bottles were then taken out, and after the precipitate had completely settled down, 25 c.c. of the solution were drawn out and poured into a strong solution of KI. The solution was then titrated with the standard thio-sulphate solution. The concentration of the halogen ion was determined by titration with $AgNO_3$ solution. The colour of $Cu^{\cdot\cdot}$ ion does not interfere with the determination of the end-point of titration in dilute solutions. For very small concentration of halogen ions, direct determination of concentration is rather difficult. It is possible however to control the concentration of halogen ion thus obtained, by calculating its values

from the concentration of $\ddot{Cu}$ ions[1]. Duplicate samples were prepared in all cases, one of which was shaken for at least an hour longer than the other ; and the results were accepted only when the two samples gave concordant results.

It is of fundamental importance to ascertain whether a real equilibrium takes place. That we get a constant value for the expression $\Sigma n \log C$ when the reaction proceeds from either side is the only convincing proof that a real equilibrium has set in. To determine this, a large quantity of pure $CuCl_2$ solution was shaken with a sufficient amount of Hg for several hours and the final strength of $\ddot{Cu}$ and Cl' ion determined. Here we have the reaction proceeding from left to right. The supernatant liquid was then decanted off and a sufficient amount of pure water put inside the bottle, which now contained Hg, Hg_2Cl_2 and CuCl. This bottle was vigorously shaken and the final strength of $\ddot{Cu}$ and Cl' ion was found to be the same.

For $\ddot{Cu}$ we get 0·0242 gram mol. per litre.

For Cl' we get 0·0484 gram mol. per litre.

Determination of the cuprous-cupric potential :— According to theory, in the reaction $2\ddot{Cu}+2Hg = \ddot{Hg_2}+2\dot{Cu}$, a real equilibrium exists only when the reacting ions have assumed such concentrations that the cuprous-cupri electrode potential becomes

(1) The calculations are made thus :—

If x and y be the initial molar contentrations of $\ddot{Cu}$ and Cl' ions and if x' be the final concentration of Cu ions, then the amount of Cl ions that has passed out of solution is given by $2(x-x')$. Therefore the final concentration of Cl' ion is $y-2(x-x')$.

equal to the potential difference existing between mercurous ion and mercury. It was thought interesting to verify this relation experimentally. A potential vessel containing a large platinised platinum electrode was complelely filled with a clear solution of copper salt in equilibrium with a mixture of CuCl, Hg_2Cl_2 and mercury, and its electrode potential against that of a deci-normal calomel electrode was measured by means of the potentiometer. The mercurous-mercury electrode potential could easily be calculated if we know the concentration of chloridion from the following equation :—

$$E = -\frac{RT}{nF}\log\frac{C}{c} = -\frac{RT}{nF}\log\frac{C.(C_{Cl'})^2}{S_1}$$

where S_1 is the solubility product of Hg_2Cl_2. We have, when $C_{Cl'} = 0{\cdot}1N$, $E = +0{\cdot}6226$ Volt at 30°C. The results are given in Table I.

TABLE I.

	Concentration of chloridion.	Observed cuprous-cupric potential.	Calculated mercurous-mercury potential.
1	0·0361 N	+0·6055 Volt	+0·6059 Volt
2	0·0484 N	+0·6026 „	+0·6020 „
3	0·0601 N	+0·5990 „	+0·5992 „
4	0·0755 N	+0·5960 „	+0·5963 „
5	0·0980 N	+0·5922 „	+0·5929 „

The agreement is fair.

TABLE II.

Results obtained when mixtures of $CuCl_2$ and KCl are shaken with mercury in presence of air.

	Molar Concentration of Cü ion.	Concentration of Cl′ ion.	$[C_{Cü}] \times C_{Cl'}]^2 = K_1$
1	0·01694	0·07276	$8 \cdot 768 \times 10^{-5}$
2	0·0099	0·7244	$1 \cdot 21 \times 10^{-4}$
3	0·0053	0·1676	$1 \cdot 49 \times 10^{-4}$
4	0·03	0·058	$1 \cdot 02 \times 10^{-4}$

It will be at once seen that the value of K_1 varies a good deal.

TABLE III.

Results obtained when mixtures of $CuCl_2$ and KCl are shaken with mercury in presence of CO_2

	Molar Concentration of Cü ion.	Concentration of Cl′ ion.	K_1.
1	0·02114	0·05174	$5 \cdot 66 \times 10^{-5}$
2	0·01985	0·05286	$5 \cdot 54 \times 10^{-5}$
3	0·01824	0·05536	$5 \cdot 58 \times 10^{-5}$
4	0·01689	0·05746	$5 \cdot 57 \times 10^{-5}$
5	0·01438	0·0637	$5 \cdot 73 \times 10^{-5}$
6	0·01209	0·0692	$5 \cdot 79 \times 10^{-5}$
7	0·0100	0·0755	$5 \cdot 70 \times 10^{-5}$
8	0·006	0·0981	$5 \cdot 75 \times 10^{-5}$
9	0·0011	0·2400	$5 \cdot 66 \times 10^{-6}$

TABLE IV.

Results obtained when mixtures of $CuSO_4$ and KCl are shaken with mercury in presnce of CO_2 gas

	Molar Concentration of Cü ion.	Concentration of Cl′ ion.	K_1.
1	0·04566	0·0361	$5{\cdot}65 \times 10^{-5}$
2	0·03937	0·03813	$5{\cdot}72 \times 10^{-5}$
3	0·03614	0·04013	$5{\cdot}70 \times 10^{-5}$
4	0·03024	0·04367	$5{\cdot}76 \times 10^{-5}$
5	0·0264	0·04644	$5{\cdot}68 \times 10^{-5}$

I will thus be seen that in presence of CO_2 gas, fairly constant values of K_1 are obtained.

The mean $= 5{\cdot}65 \times 10^{-5}$.

TABLE V.

Results obtained when mixtures of $CuSO_4$ and KBr are shaken with mercury in presence of CO_2 gas.

	Molar Concentration of Cü ion.	Concentration of Br′ ion.	K_2.
1	0·00216	0·00432	$4{\cdot}03 \times 10^{-8}$
2	0·00834	0·00222	$4{\cdot}10 \times 10^{-8}$
3	0·0223	0·00133	$3{\cdot}92 \times 10^{-8}$
4	0·0323	0·00113	$4{\cdot}12 \times 10^{-8}$
5	0·04586	0·000929	$3{\cdot}96 \times 10^{-8}$
			Mean $= 4{\cdot}05 \times 10^{-8}$

Results obtained and their discussion :—

The reaction is ionic and to obtain the exact value of the equilibrium constant it is necessary to determine the ionic concentration of Cü, Cl′ or Br′ ions. The titration values give the total copper and halogen content of the solution. To eliminate the effects due to incomplete dissociation, the concentrations of both copper and halogen ions were not allowed to exceed ·1 normal.

It is well known that CuCl and CuBr dissolve in KCl and KBr solutions respectively[1], to from complex $CuCl'_2$ ions. For dilute solutions however the effect due to formation of complex salt may be neglected.

The value of the real equilibrium constant

$$K=\left[\frac{K_1}{\sqrt{S_1}\times S_2}\right]^2 \quad \cdots \quad \cdots \quad \cdots \quad (1)$$

$$=\left[\frac{K_2}{\sqrt{S_1'}\times S_2'}\right]^2 \quad \cdots \quad \cdots \quad \cdots \quad (2)$$

The mean value of $K_1=5{\cdot}65\times10^{-5}$; S_1 the solubility product of Hg_2Cl_2 is $3{\cdot}5\times10^{-18}$. S_2 and $S'_2=1{\cdot}2\times10^{-6}$ and $4{\cdot}5\times10^{-8}$ (Bodlander. Ziet. Electrochem. 1202. **8**, 514-515); $S'_1=1{:}37\times10^{-21}$ (Sherril. Ziet. Phys. Chem. **43**, 735, 1903). $K'_2=4.1\times10^{-8}$.

The values of K obtained from equation (1) and (2) are $6{\cdot}35\times10^{20}$ and $7{\cdot}19\times10^{20}$ respectively. The agreement is very good.

1. Bödlander—Ziet Electrochem. 1902, 8, 514.

Notes on some Fish Teeth from the Tertiary Beds of Western India.

By Hem Chandra Das-Gupta m.a., f.g.s.

(with Plate I.)

The specimens that are to be described in this short note were obtained from a place called Hathab in Kathiwar. They were obtained when I had an opportunity of visiting this area in charge of a party of students from the Presidency College, Calcutta, in 1914.

The fossil-bearing locality is situated on the sea opposite to the small island of Perim, so well known for its mammalian remains. Besides Fedden's monograph(1), a few other contributions, *e.g.*, by Evans(2), Chapman (3) and Adye (4) have been published dealing with the geology of Kathiwar, but it is only in the first paper that reference has been to Hathab. Fedden gave an account of the petrology of the locality and also mentioned the fossils found by him(5). But in course of our search in the 'rag' bed of the place we obtained a richer material including the sharks' teeth to be described here. It may be pointed out that though sharks' teeth were not met with in this area previously, the Perim list includes vertebræ of shark(6).

1. *Hemipristis serra*, Agas:—Two teeth of this species have been obtained, one of medium size and

(1) Mem. Geol. Surv. Ind., vol. XXI, pp. 73-136.
(2) Quart. Journ. Geol. Soc. (Lond.), vol. 56, pp. 559-583.
(3) *Ibid.* vol. 56, pp. 584-589.
(4) Mem. Economic Geology of Navanagar State.
(5) *Op-cit.* p. 111.
(6) *Op. Cit.* p. 117.

another very small. The species has been recorded from Burma by Dr. Noetling[7] and Dr. Stuart[8] and the occurence of it in the tertiary beds of Western India is of considerable interest. The larger specimen is figured (Plate I, figs. 1, 2). The tooth is a typical upper one and, though not completely preserved, is exactly like what has been described and figured by Dr. Woodward[9] from the Parana formation (Argentine Republic).

2. *Charcharias (Prionodon) egertoni*, Agas [10] :— This species is also represented by two teeth, one of which is very small (Plate I, figs. 2, 4). It has a great similarity with *C. (Prionodon) Similis*, Probest [11]. The teeth described by Probest have, however, a root which is rather thin while those described by Agassiz have a very thick and deep root. Besides this difference in the nature of the root there appears to be another important point of distinction between the 2 species in as much as the species of Agassiz has got the teeth prominently serrated, while those described by Probest 'stehen auf der Wurzelbasis aufrecht, sind symmetrisch, gazahnett, gegen die Basis verliert sich die Zahnelung.' The Hathab teeth are prominently serrated up to the base and they can be safely referred to *C. (Prionodon) egertoni*, Agas. It may be mentioned here that this

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(7) Pal. Ind., New Ser., vol. I, Part 3, pp. 374-5, PL. XXV, figs., 9, a-e, 10.

(8) Rec. Geol. Surv. Ind., vol. XXXVIII, pp. 273, 274, 293, 297, Pl. 25, figs. 7 and 8.

(9) Ann. Mag. Nat. Hist., Ser. 7, vol. VI, P. 5, Pl. 1, figs. 11, 11a.

(10) Poiss Foss., vol. III, p. 228, Pl. XXXVI, figs. 6, 7.

(11) Württ. Jahresh., vol. 34, pp. 125-127, Taf. I, Figs. 12-19.

species has also been recorded from the tertiary beds of Burma by Dr. Stuart [12].

3. *Oxyrhina Feddeni* n. sp :—The teeth are very narrow, triangular and stand at right angles to the root. The crown is very high and very markedly curved inwards at the base and outwards towards the top. The root is fairly robust with two elongated branches diverging at an acute angle and with a very prominent vertical fissure. The present species is established on one complete tooth (pl. I figs 5, 6, 7). It has a very marked resemblance with *O. exigua* Probest[13] but differs from it in the nature of the root. It may be further added that the lower part of *O. exigua* is cylindrical while the corresponding portion in *O. Feddeni* is rather quite flat. This species has also got some resemblance with *O. spallanzani* Bon [14] but can be distinguished from it by the fact that *O. Feddeni* is comparatively narrower and the branches of the root divulge at a small angle.

PLATE I.

Figs 1-2—*Hemipristis serra*, Agas.
Figs 3-4—*Carcharias* (*Prionodon*) *egertoni*, Agas.
Figs 5, 6, 7—*Oxyrhina Feddeni* n. sp.
All natural size.

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(12) Op. cit. p. 295.

13. Wurtt. Jahresh., vol. 35, pp. 135-137, Taf. II, figs 20-25 Foldt. Kozl., vol. XXXIII, p. 156, figs 24 a-f.

14. Pal. Ind., New. Ser., vol. I, Pt. 3, pp. 372-373, pl. XXV, figs. 4, 5 a-e, 6 a-e.

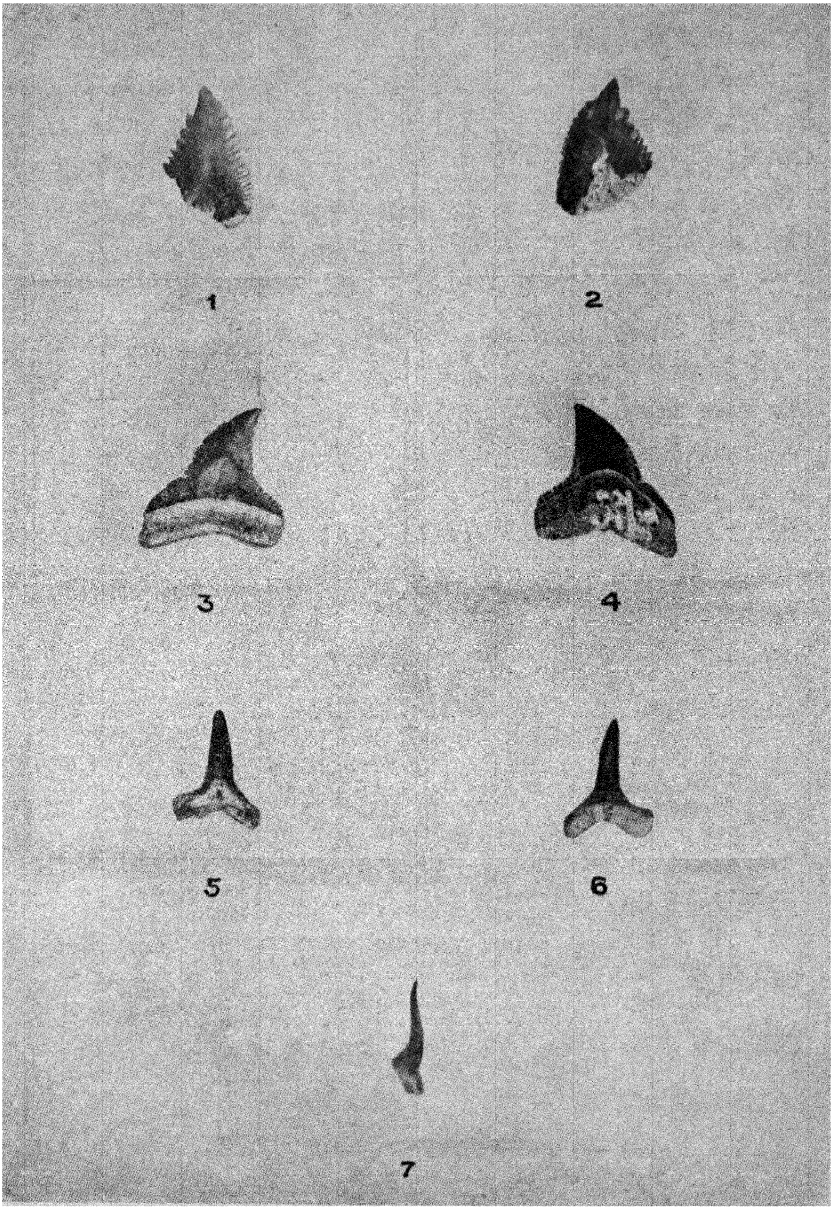

PHOTO BY B. MAITRA

FIGS. 1-2. *Hemipristis Serra*, Agas.

FIGS. 3-4. *Carcharias (Prionodon) egertoni*, Agas.

FIGS. 5-7. *Oxyrhina Feddeni* n. sp.